LABORATORY STUDY ON THE USE OF PRODUCED WATER IN CROSSLINKED-GEL-BASED HYDRAULIC FRACTURING

A Thesis

by

AHMED MOHAMED MAHMOUD ELSARAWY

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Chair of Committee,	Hisham Nasr-El-Din
Committee Members,	Zoya Heidari
	Mahmoud El-Halwagi
Head of Department,	A. Daniel Hill

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ABSTRACT

Fracturing fluids are commonly formulated with fresh water to ensure reliable fluid rheology. However, fresh water is becoming more costly, and in some areas, it is difficult to obtain. Therefore, the use of produced water in hydraulic fracturing has received increased attention in the last few years. This study investigates the feasibility of using field-produced water to formulate crosslinked-gel-based fracturing fluid through a series of laboratory experiments. Research applied three different approaches to qualify the produced water for the formulation of the fracturing fluid: 1) dilution of the produced water with fresh water, 2) reduction of water cations' concentrations, and 3) use of different chelating agents.

The fracturing fluid was prepared with the typical fluid additives used in the field. Compatibility tests were done to examine the compatibility of the water with the fracturing fluid system, and the fracturing fluid viscosity was evaluated through high-pressure high-temperature (HP/HT) viscosity measurements.

Results show that produced water could cause formation damage if used directly to formulate the hydraulic fracturing fluid. Precipitations could be prevented if the produced water is diluted with fresh water, or treated to reduce the concentration of scale-forming ions. Produced water could be used to formulate the fracturing fluid if diluted with fresh water 25 times; and the concentrations of Ca and Mg ions that the system can tolerate were found to be 400 and 25 ppm, respectively. Further reduction of divalent cations indicated the enhancement of the fracturing fluid viscosity.

The use of HEDTA and GLDA was found to increase the system tolerance to Ca and Mg ions, and to maintain adequate fracturing fluid viscosity. However, sodium gluconate, di-sodium EDTA, and di-ammonium EDTA showed a breaking effect on the viscosity of the fracturing fluid.

This work contributes to the understanding of the main factors that enable the use of produced water for hydraulic fracturing operations. Maximizing the use of produced water could reduce its disposal costs, mitigate environmental impacts, and solve fresh water acquisition challenges.

DEDICATION

I dedicate this thesis to my parents, my sisters, my brother, and my uncle. Without their love, support, and encouragement, the completion of this work wouldn't have been possible.

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CHAPTER I

INTRODUCTION AND

LITERATURE REVIEW

Hydraulic Fracturing Operation

Hydraulic fracturing has become a very common and widespread technique over the last few decades, especially after the technological advances that enabled the industry to produce from unconventional reservoirs (Parker et al. 1994; Smith et al. 1996). Hydraulic fracturing is a process to stimulate the well by creating induced fractures inside the formation that enhance reservoir productivity. This can be done by injecting a fracture fluid with a pressure higher than the formation fracture pressure. Hydraulic fracturing is used in both moderate permeability reservoirs (up to 50 md for oil reservoirs, and 1 md for gas reservoirs), and low permeability reservoirs (less than 1 md for oil reservoirs, and 0.01 md for gas reservoirs). In case of moderate permeability reservoirs, hydraulic fracturing accelerates the production without affecting the well reserves. On the other hand, hydraulic fracturing in low permeability reservoirs enhances well productivity and improves well reserves. **Figures 1 and 2** illustrate the effect of hydraulic fracturing on the production of both moderate and low permeability reservoirs, respectively (Holditch 2006).

Proppant is used to hold the induced fractures open and prevent their closure after removing the hydraulic surface pressure. Proppant is a well-sorted high-conductive grains, typically sand, that permit the flow of oil and gas towards the wellbore. **Figure 3**

illustrates the proppant placement process inside the created fractures (Economides and Nolte 2000).

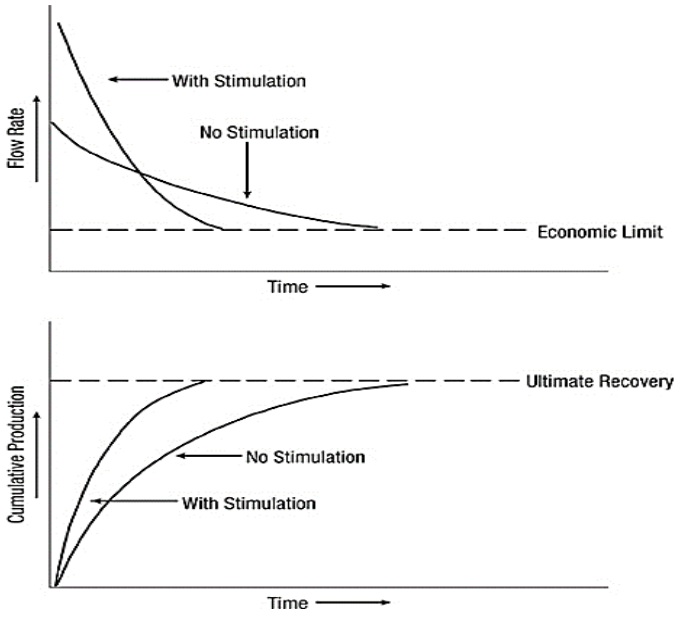


Figure 1 - Effect of Well Stimulation in Moderate Permeability Reservoirs.

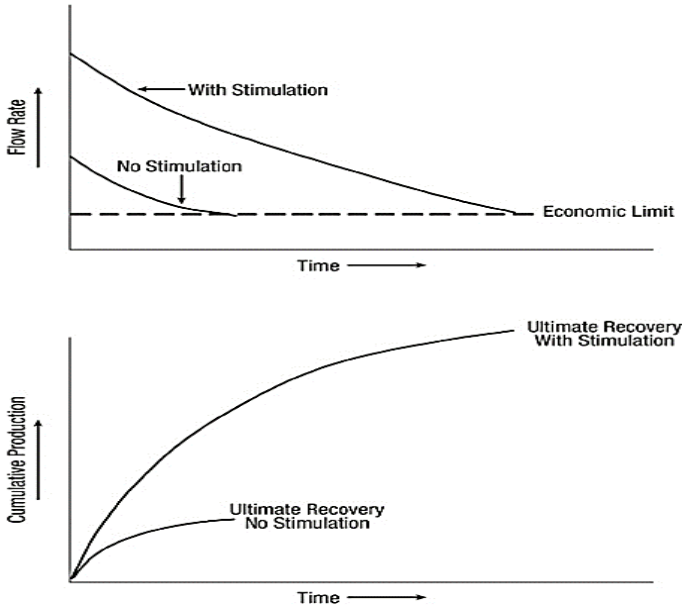


Figure 2 - Effect of Well Stimulation in Low Permeability Reservoirs.

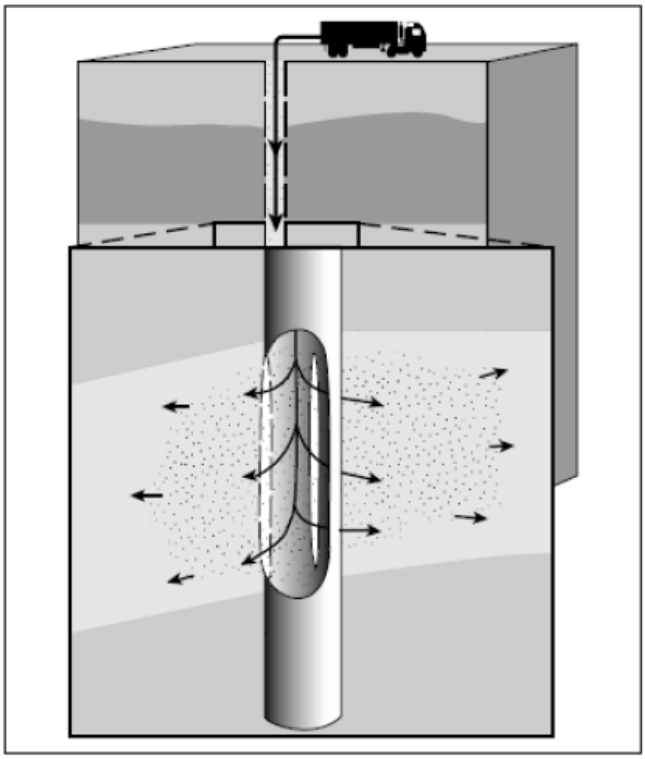


Figure 3 - Proppant Placement Inside the Fracture.

The design of the fracturing fluid is a very important factor that determines the success or failure of hydraulic fracturing treatments. Fracturing fluid should 1) has the necessary viscosity for carrying the proppant at reservoir pressure, temperature, and the expected shear conditions, 2) be save: to personnel and to environment, and 3) easily broken: for high flow back efficiency and minimize formation damage potentials. Excessive fluid viscosity would increase the required surface pressure, increase the treatment costs, and would cause formation damage and reduced fracture conductivity. Insufficient viscosity would cause the proppant to settle inside the wellbore, increase

fluid loss into the formation, and induce insufficient fracture width. Roles of viscosity in hydraulic fracturing (Economides and Martin 2007):

1. creates the necessary fracture width for proppant entrance into the fracture
2. transports the proppant from the wellbore to the fracture tip
3. controls the fluid loss into the formation
4. controls the pressure to ensure proper fracture height and fracture growth.

Hydraulic Fracturing Fluids

Water-base fluids are the most commonly used fracturing fluids due to their low cost, high performance, and ease of handling. Water can be used alone in hydraulic fracturing without any source of viscosity, in which the fracturing fluid is composed only of water and a friction reducer. This technique is called Water Frac. Water recovery agent can also be added to improve the fracturing fluid recovery and prevent water blocking problems after the treatment. This type of fracturing is commonly used for shale formation. The main advantage of this technique is the low viscosity of the fracturing fluid which results in a very narrow fracture width. Proppant transport is controlled by the fluid pumping rate. In order to avoid proppant settling, the fluid should be pumped at very high rates (60 to 120 bpm). **Table 1** summarizes the advantages and disadvantages of this technique.

Table 1 - Advantages and Disadvantages of Water Frac Technique.

Advantages	Disadvantages
Low cost	Low fluid viscosity
Easy to be mixed	Small fracture width
High flow back efficiency	Require high pumping rate to transport the proppant (60-120 bpm)
Ability to reuse the flow back water	low fluid loss control

Linear gel fluid is composed of water and gelling agent, such as guar polymer. The main advantages of the linear gel is its low cost and improved viscosity characteristics. Fluid loss to the formation is controlled by the filter cake formation at the face of the formation. The flow back fluid after the treatment usually contains the polymer residues, which make its use in further operations more difficult than water fracturing operations. **Table 2** summarizes the advantages and disadvantages of using linear gel fracturing fluid.

Crosslinked gel is the fracturing fluid contains water, gelling agent and a crosslinker. Crosslinker can be added to the fracturing fluid to link the polymer molecules together and increase the fluid viscosity into the 100's or 1000's of cps range. Higher fluid viscosity increases the created fracture width, as a results, increases the proppant concentration inside the fracture. Furthermore, high fluid viscosity would

decrease the fluid loss to the formation and improve fluid recovery during the flow back process. **Table 3** summarizes the advantages and disadvantages of the crosslinked gel fracturing fluids.

Table 2 - Advantages and Disadvantages of Using Linear Gel Fracturing Fluid.

Advantages	Disadvantages
Low cost	Narrow fracture width
Improved fluid viscosity (10-60 cp)	Water produced needs further treatment
Fluid loss controlled by the filter cake formed along the fracture face	

Oil base fracturing fluid is used with formations that are very sensitive to water. Water can cause formation damage when it comes in contact with water-sensitive formations. It is worth to mention that the first fracturing fluid used in the history was oil base fluid. The fluid consisted of gasoline as the base fluid, palm oil as the gelling agent, and naphthenic acid as the crosslinker. There are many restrictions on the use of oil base fracturing fluid as it is environmentally unfriendly and can cause safety hazards. Besides, if refined oil such as diesel, is used as the base fluid, the cost of the operation would be very high.

Table 3 - Advantages and Disadvantages of Using Crosslinked Gel Fracturing Fluid.

Advantages	Disadvantages
High fluid viscosity, can reach 100's and 1000's cp	Water produced needs further treatment
Higher fracture width	
Improve proppant transport	
Reduce fluid loss	

Emulsion fluid (water in oil or oil in water) can be used as hydraulic fracturing fluid in the presence of an emulsion stabilizer, such as surfactant. The most commonly used type of emulsion is called polyemulsion, and it is composed of 67% hydrocarbon internal phase, 33% brine external phase, and an emulsifying surfactant. The polymer concentration used with emulsion fluid is one-sixth to one-third of that used with standard water-base fracturing fluid. As a result, emulsion fluid is known to cause less formation damage and better cleaning up process. Emulsion fluid also provides good fluid loss control and high proppant carrying capacity. The viscosity of the fluid can be controlled by hydrocarbon to water ratio.

Foam, as a fracturing fluid, is usually used with low pressure reservoirs as it can significantly improve the fluid flow back efficiency. Foam is a stable mixture of liquid and gas. Carbon dioxide or nitrogen gases are the commonly used gases to form the fluid. Surface active agent should be used to stabilize the thin film between the liquid

and gas phases. The use of foam as a fracturing fluid can reduce the contact between the liquid phase and the formation, thus, it can be used with water-sensitive formations. The low density of the fluid makes its recovery easier, especially in low pressure reservoirs where there is no enough pressure to flow back the fluid to the surface. The use of foam depends on the availability of gas at the well site and the available surface pressure to be used for fluid injection.

Fracturing Fluid Additives

Various additives are used in hydraulic fracturing operations. The choice of each additive should be done carefully to ensure its compatibility with the fluid system. Fluid additives have different properties and function. The main component in the fracturing fluid is the gelling agent, which is the main source for fracturing fluid viscosity. Guar polymer is the most commonly used gelling agent in hydraulic fracturing operations (Al-Muntasheri 2014). Guar is a long-chain co-polymer that consists of a mannose sugar backbone with galactose sugar side chains. These side chains are randomly arranged along the mannose sugar backbone. The ratio of the mannose to galactose units is about 2:1. The average molecular weight of guar ranges upwards from 1.5 million g/gmol and is a nonionic molecule (Jennings 1996). **Figure 4** shows the typical molecular structure of guar polymer. The world's production of guar is focused in India, Pakistan, and the United States, with limited quantities in South Africa and Brazil. The primary growing regions in the US are Texas, Oklahoma, and Arizona. The seed is planted in May or June and harvested in October or November. After harvesting the seed, the coat and germ are removed to form what is called a Guar Split. The Guar Split is then grounded to form the

guar powder. The diagram in **Figure 5** explains the manufacturing steps of the guar powder.

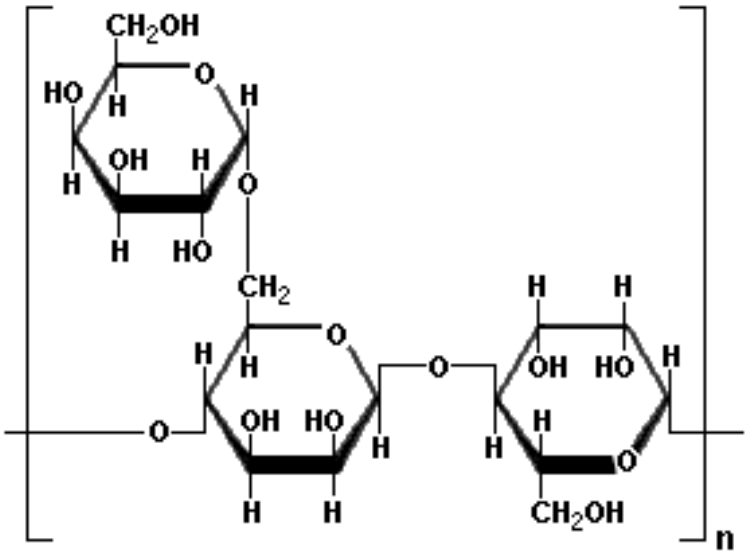


Figure 4 - Guar Molecular Structure.

When the guar polymer is broken, it leaves from 6 to 10 % insoluble residues, which could cause formation damage and reduce the flow back efficiency. Guar derivatives have been introduced to reduce polymer insoluble residues, increase stability at elevated temperature, and maintain gel viscosity at low pH environments. The most common types of Guar derivatives are Hydroxypropyl guar (HPG), Carboxymethyl guar (CMG), and Carboxymethyl Hydroxypropyl Guar (CMHPG). The derivatization of guar to form HPG occurs through the reaction of sugar hydroxyls with base and propylene oxide, while the CMG can be formed by the reaction of guar with chloroacetic acid. **Figure 6** shows the chemical structure of both HPG and CMG.

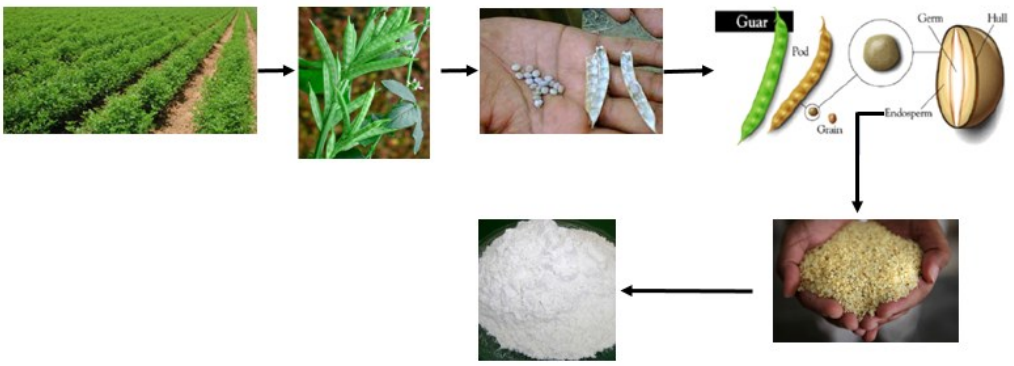


Figure 5 - Manufacturing Process of Guar Powder.

A care must be taken when mixing Guar polymer with the fluid system. It should be added gradually and maximum mixing energy should be used to ensure proper polymer distribution inside the solution and to avoid forming clumps, which are known as “fish eyes”. Fish eyes are formed due to the hydration of the outer part of the polymer, which prevent further water contact with the inner part of the polymer.

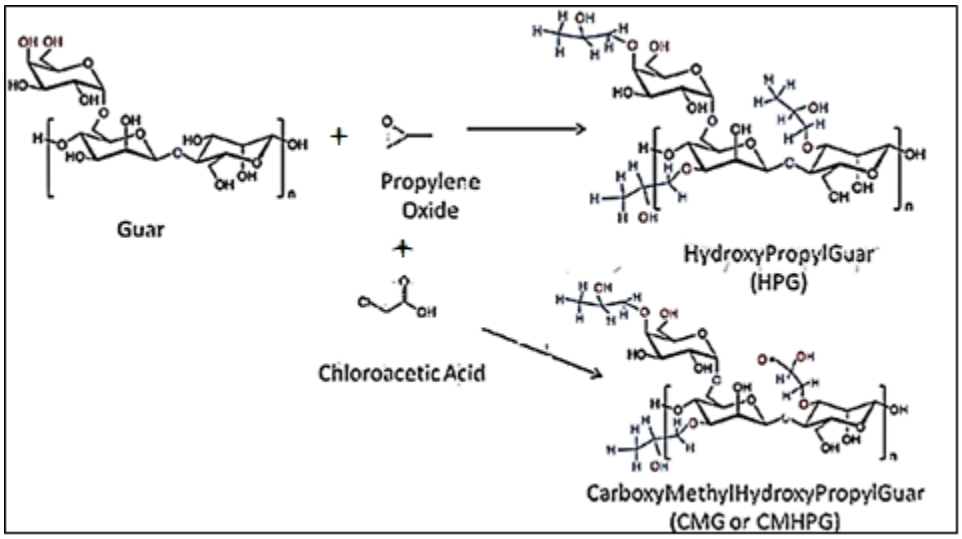
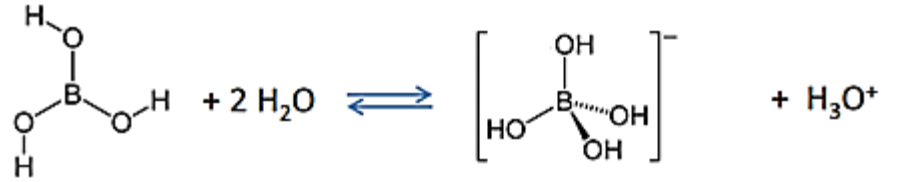


Figure 6 - Molecular Structures of HPG and CMG.

Crosslinkers are used to increase the viscosity of the fracturing fluid by crosslinking the polymer molecules together, which can increase the viscosity to 1000's cp. Common crosslinkers are metal-based crosslinkers, such as boron (B), titanium (Ti), zirconium (Zr), and aluminium (Al). Crosslinking time can vary from one type to another. Delayed crosslinking can reduce the friction pressure inside the wellbore and provide the necessary viscosity inside the fractures. Borate ion $(B(OH)_4)^-$, the crosslinking species of the boron ion, can provide a very viscous and stable fluid at temperature up to 300 ^{O}F. The optimum pH value for the crosslinking process is between 10 and 12, depending on the borate compound and borate ion concentration (Harris 1993). High pH value is required to maintain adequate concentration of borate ions in solution. The chemical structure of borate crosslinked guar is shown in **Figure 7**. Borate ions can be formed by the reaction between boric acid and water as follows.



Boric acid **water** **Tetrahydroxyborate anion** **proton**

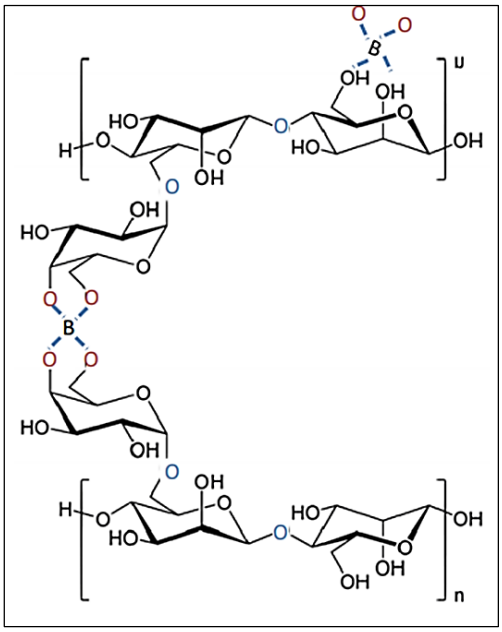


Figure 7 - Guar Molecules Crosslinked with Borate Ion.

Biocides are added to the fracturing fluid to prevent the biological degradation of the fluid gelling agent, which leads to a significant decrease in the fluid viscosity. In addition, some anearobic bacteria can reduce sulfate ions to H_2S, extremely dangerous gas. Glutaraldehyde, chlorophenates, quaternary amines, and isothiazoline are the most commonly used biocides.

Surfactants have many functions when used in hydraulic fracturing operations. Surfactants reduce interfacial tension and capillary pressure in the pore spaces. Therefore, they enhance the fluid flow back efficiency, which could reduce the formation damage and enhance oil and gas relative permeabilities. In addition, surfactants can prevent the formation of emulsion and can be used as a stabilizer for nitrogen or carbon dioxide gases to prepare foam fracturing fluid. Surfactant types are

cationic, anionic, or nonionic. Compatibility of the surfactant with other fracturing fluid additives should be tested prior to its use.

Friction reducer can be added to the fracturing fluid to reduce the friction pressure between the fluid and pipe surface. Friction reducer helps to maintain laminar flow and decrease turbulent flow period. Laminar flow results in a lower friction pressure, thus, reduce the required fluid pumping surface pressure. Polyacrylamides are the commonly used friction reducer, which is typically dispersed in a hydrocarbon carrier.

Clay controllers are used to stabilize clays and prevent its swelling. Clay swelling and fine migration can block the pore throats and cause formation damage. Potassium chloride (1 wt% to 3 wt%) is usually used to control clays and fine migration. Quaternary amines and inorganic polynuclear cations are used as a permanent clay controller and maintain the chemical environment of the clay particles. Quaternary amines contain a positively charged group that is attracted to the clay particles and cause clay stabilization. This type of clay controller is usually used with water base fracturing fluids.

Buffers are used to adjust the fluid pH value. Fluid pH value controls the hydration of the gelling agent, the crosslinking process, and the fluid breaking time. Fluid pH value should be adjusted to the optimum value based on the type of the fracturing fluid system. The pH value can be adjusted using most acids and bases. Common buffers include sodium hydroxide, acetic acid, sodium carbonate, and potassium carbonate.

Scale inhibitor is usually used to prevent scale formation in the wellbore and inside the formation. Scale inhibitor can prevent scale formation due to the mixing of formation water with the fracturing fluid. The selection of the type of the scale inhibitor depends on the properties of both the fracturing fluid and the formation fluids.

For the success of the hydraulic fracturing operation, fracturing fluid prepared with produced water should show a sufficient viscosity to properly place the proppant into the created fractures. In addition, fluids should be broken easily to a low viscosity after the treatment is done to ensure high fracture and proppant pack conductivity. Breakers are added to the fluid formulation to break the fluid after the treatment is complete. Oxidizers and enzymes are used to degrade guar-based fracturing fluids. Oxidizers (persulfates) degrade the polymer through a free radical reaction with sulfur. This reaction reduces the molecular weight of the polymer by breaking the large molecules into shorter ones. A reduction of polymer molecular weight will lead to a significant reduction in the fluid viscosity. On the contrary, enzymes break the polymer by hydrolysis of polymer chains. The fluid breaking rate should be optimized; and it depends on many factors, including the following: breaker type and concentration, fluid composition and pH value, and reservoir temperature (Almond 1982).

The Use of Produced Water in Hydraulic Fracturing

Different approaches have been utilized in the literature to enable the use of produced water in hydraulic fracturing operations. Huang et al. (2005) showed the feasibility of the direct use of produced water to formulate crosslinked-gel-based fracturing fluid in New Mexico. Polymer hydration and water pH value were found to

significantly affect the fluid viscosity and should be optimized based on the laboratory studies. Li et al. (2009) presented a new fluid stabilizer that can prevent the damaging effect of produced water bacteria and bacterial enzymes. The new stabilizer has enabled the use of produced water for preparing polysaccharide-based fracturing fluid, which has reduced the amount of fresh water used and thus reduced the operating cost. Fedorov et al. (2010) has presented a case study on using produced water for hydraulic fracturing in Western Siberia. The study used a chelating agent and modified the water's pH value to successfully formulate fracturing fluid with a reliable rheology.

LeBas et al. (2013) presented the use of the Electro-Coagulation (EC) method for produced water treatment to qualify the produced water for fracturing fluid formulation. In EC, an electric current is applied across metal plates to remove various contaminants from the water. Heavy metals (ions) and colloids (organics and inorganics) are primarily held in solution by electrical charges and particle size. The electrical charge applied to the solution of contaminated water destabilizes the charges on the particles and generates a coagulation reaction. This step in the recycling program removes specific contaminants, including suspended solids, which allows the treated water to be used in future fracturing applications. Treated produced water was used to prepare guar-based fracturing fluid crosslinked with zirconium ions, and the fluid was used to fracture seven wells with 97 fracturing stages. Kakadjian et al. (2013) presented a new zirconate cross-linked fracturing fluid system. The system enabled the use of 100% untreated produced water to formulate the fracturing fluid, which has saved the use of three million gallons of fresh water during the completion of two wells in the Bakken field. Fedorov et al.

(2014) proposed a new scale inhibitor that can prevent scale formation by sequestering cationic scale-forming ions. The new scale inhibitor has been added to the fracturing fluid recipe, which enabled the use of produced water to implement 200 stages of hydraulic fracturing in West Texas. Li et al. (2015) introduced two novel additives that can prevent formation damage that could be formed as a result of the high hardness level of produced water. At the right concentration, the additives have improved the viscosity of organomettalic crosslinked derivatized polysaccharide fluid two times.

Problem Description

Hydraulic fracturing requires a large amount of water to formulate the fracturing fluid. The amount of water required for the operation varies according to the well type and number of fracturing stages. Conventional vertical wells may require as little as 500,000 gallons of water, while in multistage horizontal well fracturing, water consumption can reach two to four million gallons. **Table 4** shows the average use of water per well in multi-stage hydraulic fracturing of horizontal wells for different shale plays in the United States (US Department of Energy, 2009).

Table 4 - Average Use of Water per Well in Multi-Stage Hydraulic Fracturing of Horizontal Wells.

Shale Gas Play	Average Water Consumption per Well in Multi-Stage Fracturing of Horizontal Wells
Barnett Shale	2,300,000 (gallons)
Fayetteville Shale	2,900,000 (gallons)
Haynesville Shale	2,700,000 (gallons)
Marcellus Shale	3,800,000 (gallons)

Fracturing fluid is usually formulated with fresh water from surface and subsurface sources. Obtaining fresh water has become a challenge in some fields due to the high water transportation costs from its source to the well site, in addition to increasing restrictions on the fresh water availability (Gleick 1994). On the other hand, most fields produce a high amount of water accompanying oil and/or gas production, and, in some cases, produced water volume can be several times that of hydrocarbons produced (Stephenson 1992). Purder (2007) reported that 18 billion barrels of produced water were disposed of or treated at well sites across the United States.

Produced water generally consists of formation water, flowback water from previous well treatments, and surface water. It usually contains hydrocarbons, high levels of salts and hardness, suspended solids, residual production chemicals, and bacteria. Produced water can be environmentally hazardous and is thus treated or

disposed of following strict environmental regulations. The average cost of disposal through injection wells ranges from $0.30 to $10.00/bbl, while disposal through solidification and burial in a landfill can cost up to $22.00/bbl (Puder 2007).

To address the challenges of fresh water acquisition and produced water disposal, the use of produced water in hydraulic fracturing has received increased attention in the last few years. The high TDS content and the high levels of divalent cations (mainly Ca and Mg) of the produced water are the main factors that inhibit its use in the formulation of the fracturing fluid. The high TDS content affects the hydration of polymers, the main viscosity-building source (Bemiller 1992). High concentrations of Ca and Mg ions could cause precipitations at high pH environments, which could cause formation damage and reduce well productivity.

Objective

The objective of this study is to experimentally investigate the feasibility of using field produced water to formulate the hydraulic fracturing fluid through 1) dilution of the produced water with fresh water, 2) reduction of water cations' concentrations, and 3) the use of chelating agents.

This study contributes to the understanding of the main factors that enable the use of produced water for hydraulic fracturing operations. The use of produced water in hydraulic fracturing could save its disposal cost, mitigate environmental impacts, and solve fresh water acquisition challenges.

CHAPTER II

EXPERIMENTAL STUDIES

The objective of this study is to investigate the use of field produced water samples to prepare crosslinked-gel-based hydraulic fluid. The following procedures were followed in the study:

1. Field produced water sample was filtered and analyzed.
2. Fracturing fluid with typical field additives was prepared using the produced water as a base fluid.
3. Compatibility tests were done to evaluate the formation damage that could happen due to system incompatibility.
4. Fracturing fluid viscosity was evaluated using high pressure high temperature viscosity measurements.
5. Produced water was diluted with fresh water and tested at different dilution factors.
6. Synthetic produced water was prepared and the effect of reduction of each ion concentration was tested.
7. The effect of adding chelating agents to the fluid system was examined.

Materials

All materials used for this study were provided by a local service company. Materials used were guar polymer, borate cross-linker, pH buffer, micro-biocide, non-ionic surfactant, clay controller, scale inhibitor and gel breaker. The chemical composition of each additive is shown in **Table 5**.

Table 5 – Chemical Composition of Fracturing Fluid Additives.

Additive	Chemical Composition
Micro-biocide	- Aqueous glutaraldehyde - Quaternary ammonium chloride
Non-ionic surfactant	- Methanol (30-60 wt%) - Isopropyl alcohol (10-30 wt%) - Ethylene glycol (10-30 wt%) - Ethoxylated alcohol (1-5 wt%) - Alkoxylate (1-5 wt%) - Nonylphenol ethoxylate (0.1-1 wt%)
Guar polymer	- Guar gum - Petroleum Distillates
Clay controller	- Quaternary salts (30-60 wt%)
Scale inhibitor	- Methanol (5-10 wt%) - Nonylphenol ethoxylate (5-10 wt%)
High pH buffer	- Sodium hydroxide (20-35 wt%)
Crosslinker	- Potassium metaborate - Potassium hydroxide - Ethylene glycol

NaCl, KCl, $CaCl_2.2H_2O$, $MgCl_2.6H_2O$ and Na_2SO_4 were used as sources for Na^+, K^+, Ca^{+2}, Mg^{+2} and SO_4^{-2} ions, respectively. All salts are American Chemical Society (ACS) grade and used as received from a supply company. De-Ionized (DI) water, with a resistivity of 18.2 MΩ.cm at room temperature, was used to prepare all fracturing fluids.

Equipment

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

Produced water samples was filtrated and analyzed using an Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) apparatus, shown in **Figure 8,** to determine the cations' concentrations. Optical Emission Spectroscopy (OES) determines the analyte concentration using quantitative measurements of the optical emission from the excited atoms. Analyte atoms in solution are moved to the excitation region where they are desolvated, vaporized, and atomised by a plasma. When the energy is applied to the atom, the electron can gain energy and move to the upper electron orbit (the excited state), while the un-energized electron stays in the ground state. When the electron returns back to its ground state, a photon of light is emitted. A unique set of wavelengths are emitted for each specific type of element. An illustration of the theory is given in **Figure 9.**

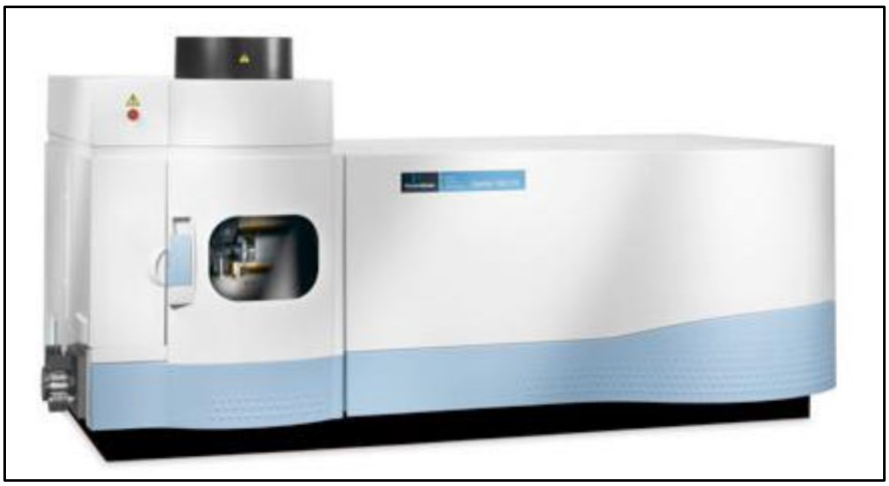


Figure 8 - Inductively Coupled Plasma Optical Emission Spectrometry Device.

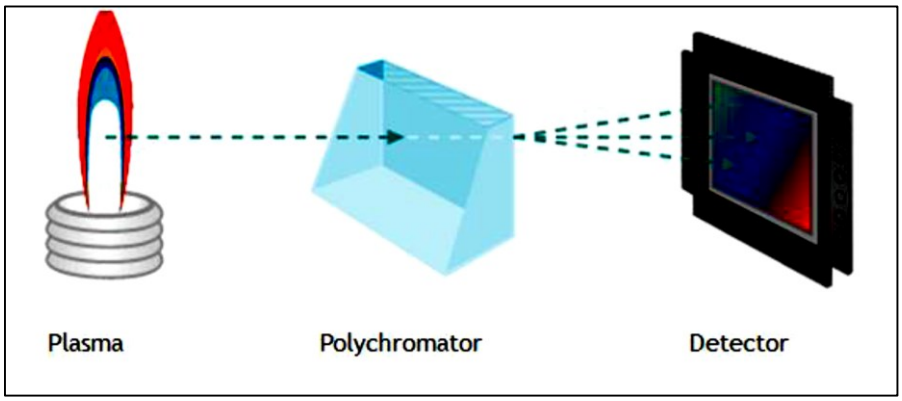


Figure 9 - An Illustration of ICP-OES Theory

High Pressure High Temperature (HP/HT) Rheometer

The apparent viscosity of the fluid was measured using a Grace M5600 high pressure high temperature rotational rheometer shown in **Figure 10**. The Grace Instrument M5600 HP/HT rheometer is an Couette, coaxial cylinder, rotational, high pressure and temperature rheometer (up to 1,000 psi and 500 °F). All tests were done at a temperature of 180 ^{O}F and pressure of 300 psia. All tests were conducted with B5 bob and 52 ml fluid volume.

Figure 10 - HP/HT Rotational Rheometer.

Experimental Procedures

Water Analysis

Produced water samples were collected from the field. The samples were filtered and analyzed using Inductively Coupled Plasma (ICP) to determine the cations' concentrations. A spectrophotometer was used to determine the sulfate concentration. Bacterial analysis was done by a third party.

Synthetic Water Preparation

Certain amounts of salts were added to DI water according to the required concentration of each ion. Five salts were used: NaCl, KCl, $CaCl_2.2H_2O$, $MgCl_2.6H_2O$, and Na_2SO_4, as a source for Na^+, K^+, Ca^{+2}, Mg^{+2}, SO_4^{-2} ions, respectively. The water was allowed to mix for 15 minutes using an overhead mixer to ensure salts dissolution.

Fracturing Fluid Preparation

All fluids were prepared according to the formulation shown in **Table 6**. Concentration of each additive was chosen based on industry-standard values used in the field. All concentrations are shown in gpt unit (gallon per thousand gallons).

Table 6 - Formulation of the Fracturing Fluid.

Additive	Concentration (gpt)
Micro-biocide	0.3
Surfactant	1.0
Guar polymer	4.5
Clay controller	1.0
Scale inhibitor	0.15
High pH buffer	1.5
Crosslinker	2.0

The following procedures were used to prepare all fluid samples:

1. Certain amounts of salts were added to 250 ml DI water according to the required concentration of each ion. Five salts were used: NaCl, KCl, $CaCl_2.2H_2O$, $MgCl_2.6H_2O$, and Na_2SO_4.
2. The water was allowed to mix for 15 minutes using an overhead mixer to ensure salts dissolution.
3. The fracturing fluid was preconditioned before placement in the viscometer by mixing in a waring blender.
4. The biocide and surfactant were added to the water, followed by the guar polymer.
5. The fluid was then allowed to hydrate for 2 minutes and 40 seconds.
6. The clay controller and scale inhibitor were then added.

7. The high pH buffer was added to increase the pH value to 11. A high pH value is required for borate-based crosslinkers.
8. The crosslinker was finally added and continuously mixed until gel crowning occurred (15 to 30 seconds).
9. Air bubbles trapped inside the fluid were removed by centrifuge at 6,000 rpm for 5 minutes.

Viscosity Measurements

The apparent viscosity of the fluid was measured using a Grace M5600 HP/HT rotational rheometer. All tests were done at a temperature of 180 ^{O}F and pressure of 300 psia. Tests were performed at a constant shear rate of 100 sec^{-1} with shear ramps (75, 50, 25, 50 and 75 sec^{-1}) repeated every 30 minutes. The test duration was 3 hours or until fluid viscosity dropped below 25 cp at 100 sec^{-1}. All tests were conducted with B5 bob and 52 ml fluid volume. Test primary steps and ramp steps are shown in **Tables 7 and 8**, respectively.

Table 7 – Viscosity Measurements Primary Steps.

Step	Shear rate (sec^{-1})	Time (mins)	Temp (^oF)	Error in Temp (^oF)	Ramp
1	100	30	180	5	1
2	100	30	180	5	1
3	100	30	180	5	1
4	100	30	180	5	1
5	100	30	180	5	1
6	100	30	180	5	1

Table 8 - Viscosity Measurements Ramp Steps.

Shear rate (sec^{-1})	Time (sec)
75	90
50	90
25	90
50	90
75	90

Compatibility Tests

Compatibility tests were done to test the compatibility of the base water with the fracturing fluid additives. The fracturing fluid was prepared using the base water and the complete fluid additives. Then, 100 ml of the fluid was put in the oven at 180 ^{O}F. The sample was observed for precipitations after three hours.

CHAPTER III

RESULTS AND DISCUSSION

Produced Water Analysis

Analysis of the produced water samples showed a total TDS content of 125,000 ppm, including: Na, K, Ca and Mg ions concentrations of 36,000, 1,700, 10,500 and 700, respectively. Sulfate concentration was found to be 95 ppm. Bacterial analysis showed a bacteria concentration of 41,370 ME/ml. **Table 9** summarizes the chemical analysis of the produced water.

Table 9 - Chemical Analysis of the Produced Water.

Parameter	Value
Specific gravity	1.08
pH	4
Bacteria (ME/ml)	41,370
TDS (mg/l)	125,000
Na+ (mg/l)	36,000
K^{+} (mg/l)	1,700
Ca^{+2} (mg/l)	10,500
Mg^{+2} (mg/l)	700
SO_4^{-2} (mg/l)	95

Direct Use of Produced Water to Prepare the Fracturing Fluid

Fracturing fluid was formulated using the produced water as a base fluid. Precipitations were observed after the addition of the high pH buffer to the system. The high pH buffer is sodium hydroxide and is used to raise the pH value to 11 in order to generate sufficient borate ions to adequately crosslink the polymer molecules. The increase in the pH value causes the precipitation of divalent cations as insoluble hydroxides and lead to reduction of the pH value of the system. ICP analysis was performed on the solution before and after the precipitation. Results in **Table 10** showed the reduction of Ca ion concentration which indicated the precipitation of calcium out of the solution as $Ca(OH)_2$.

Precipitates were separated and the fracturing fluid was formed after the separation. The viscosity profile of the fluid is presented in **Figure 11**, which shows initial viscosity of 85 cp and dropped to 20 cp after 38 minutes. The fluid showed a low and unstable viscosity profile due to the low pH value of the system. The pH value was measured and found to be 5.5, which is insufficient for polymer crosslinking, and as a result, a low viscosity profile was observed.

Table 10 - ICP Analysis of the Solution Before and After Precipitation.

Element	Concentration before precipitation (mg/l)	Concentration after precipitation (mg/l)
Ca^{+2}	12,500	10,000
Na^{+1}	36,000	36,000
K^{+1}	1,700	1,700
Mg^{+2}	700	700

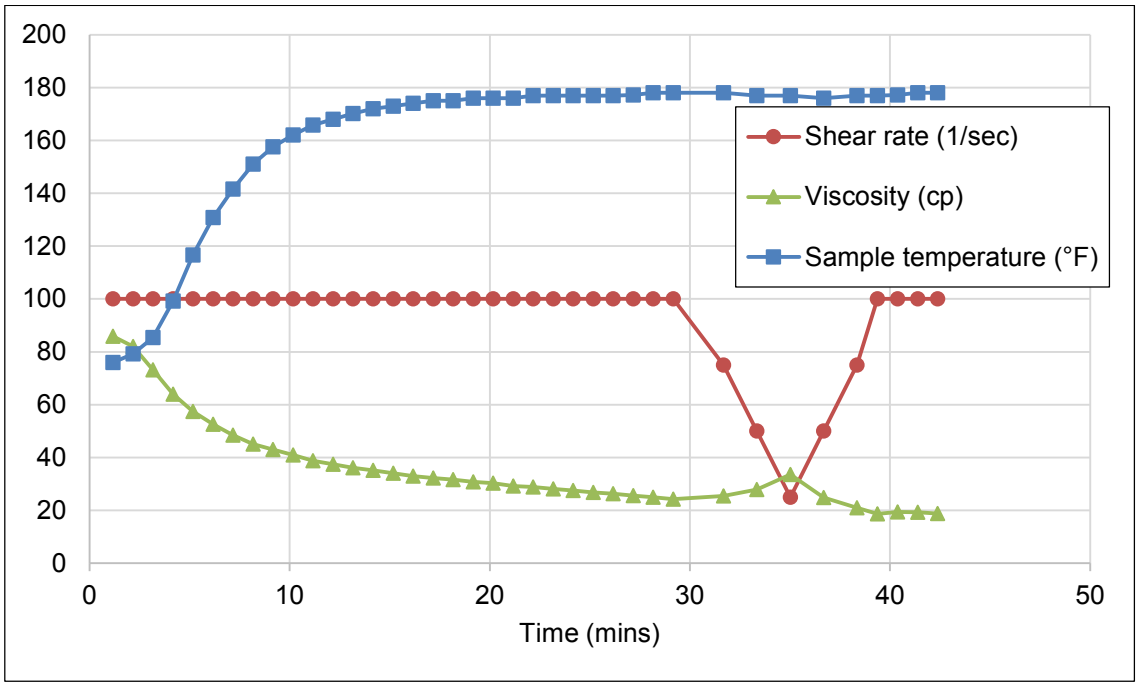


Figure 11 - Viscosity Measurements of the Fluid Prepared With Produced Water.

To avoid the formation of precipitation and ensure a reliable fracturing fluid rheology, produced water ion concentrations should be reduced. Dilution of the produced water with fresh water represents the first approach for direct use of produced water (without treatment) for preparing the fracturing fluid. The fracturing fluid is currently formulated in the field using fresh water from a nearby pond. Fresh pond water samples were obtained and firstly used to formulate the fracturing fluid to establish a baseline performance for viscosity measurements.

Fresh water was used to dilute the produced water at different dilution factors (10, 15, 20 and 25) and the diluted produced water was then used to formulate the fracturing fluid. Compatibility results in **Table 11** indicated that the produced water should be diluted at least 25 times in order to avoid the precipitations and formation damage. The viscosity of the fluid prepared with the diluted produced water (25 times) was examined, and the fluid showed a stable viscosity of more than 200 cp for the three hours test duration. **Figure 12** shows the comparison between the viscosity profile of the fluid prepared with diluted produced water 25 times and the fluid prepared with fresh water.

Table 11 - Compatibility Results of Fluid Prepared with Diluted Produced Water

Experiment	Dilution Factor	Na^{+1} (mg/l)	K^{+1} (mg/l)	Ca^{+2} (mg/l)	Mg^{+2} (mg/l)	Results
1	10	3,600	170	1,050	70	Precipitates were observed
2	15	2,400	113	700	46	Precipitates were observed
3	20	1,800	85	525	35	Precipitates were observed
4	25	1,440	68	420	28	No Precipitates were observed

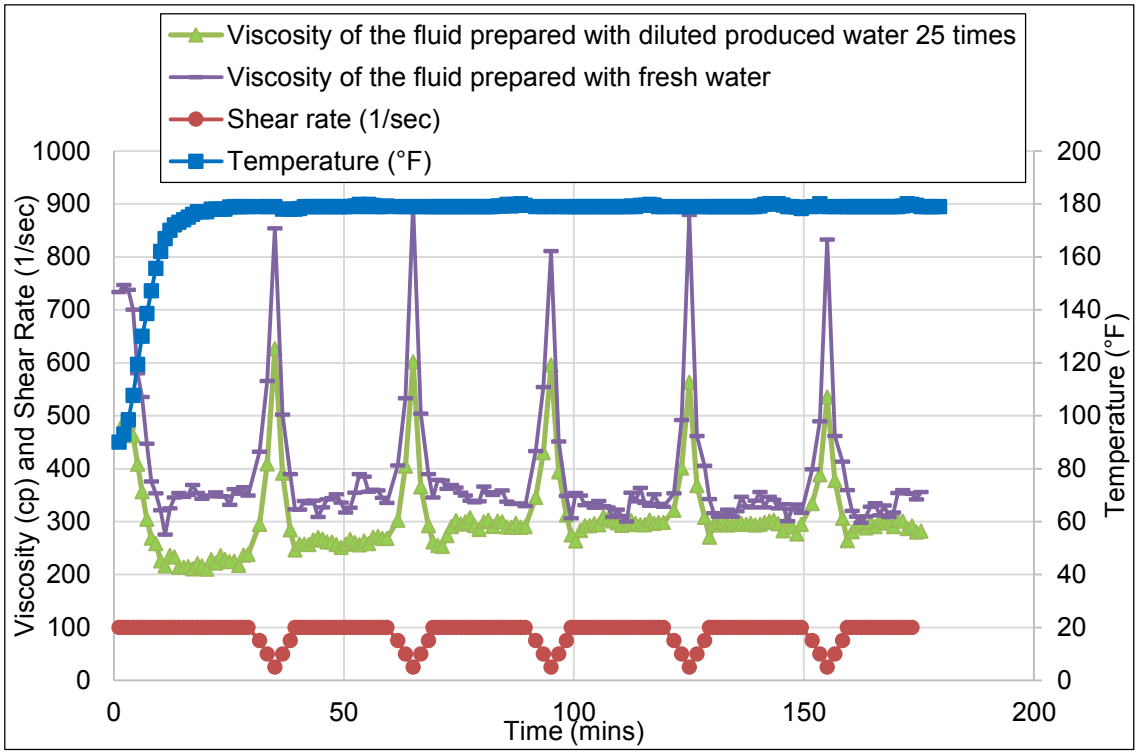


Figure 12 - Comparison between the Viscosity Profiles of the Fluid Prepared with Diluted Produced Water 25 times and the Fluid Prepared with Fresh Water.

Formulation of Synthetic Produced Water and Prevention of Divalent Cations Precipitation

Water treatments (on-site or off-site treatments) provide another approach to reduce produced water ions' concentrations. The effect of reduction of each ion on both the precipitate formation and the viscosity of the fracturing fluid were studied. To control the different water ions concentrations in the system, synthetic produced water was prepared using DI water and varying amounts of NaCl, KCl, $CaCl_2$, $MgCl_2$, and Na_2SO_4 salts. Synthetic water with Na, K, Ca, Mg and SO_4 concentrations of 36,000, 1,700, 10,500, 700 and 95 ppm was prepared to simulate the actual produced water. Synthetic produced water was then diluted 25 times and was used to prepare the fracturing fluid, and fluid viscosity was then measured.

Results in **Figure 13** show the viscosity profile of the fluid prepared with diluted synthetic produced water and diluted actual produced water (both diluted 25 times). Results indicate a good agreement between the two profiles, which indicates that the synthetic produced water can resemble the actual produced water. Bacteria and other components in the produced water showed no effect on the viscosity profile and can be neglected for comparison purposes. Bacteria is known in the literature to affect fluid viscosity due to its biodegradation effect. However, due to its low concentration, it showed no effect on the fluid viscosity for the three hours of the test duration.

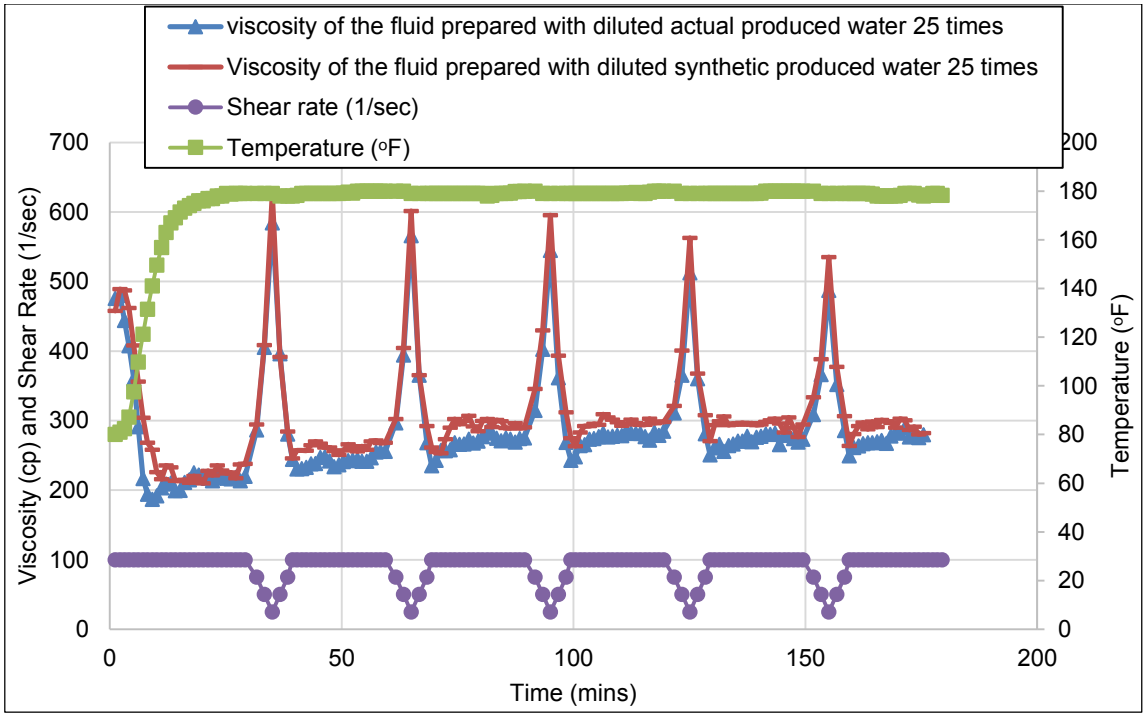


Figure 13 - Viscosity Measurements of the Fluid Prepared with Diluted Produced Water and Diluted Synthetic Produced Water.

Synthetic produced water was then used to formulate the fracturing fluid. The same precipitate was formed as the precipitate observed with the actual produced water. To avoid such precipitate, concentrations of divalent cations (Ca and Mg) in the water were reduced gradually to determine the concentration of both ions that the system can tolerate. The concentration of ions in the system was controlled by regulating the amount of each salt in the base water. Compatibility results in **Table 12** confirmed that Ca and Mg ions are the sources of precipitation and should be reduced to 400 and 25 ppm, respectively. These values are the maximum concentrations of Ca and Mg ions that the system can tolerate and they are consistent with the results shown previously in **Table 11.** The viscosity of the fluid prepared with synthetic produced water with a reduced

amount of Ca and Mg ions (400 and 25 ppm, respectively) was then measured and results are shown in **Figure 14**. **Table 13** presents the composition of water used to prepare the fluid. The viscosity profile indicated the reduction of fluid viscosity compared to the base line viscosity profile of the fluid prepared with fresh water.

The reduction of Ca and Mg ion concentrations to 400 and 25 ppm, respectively, has prevents the formation of precipitate and has enabled the formulation of the fracturing fluid with a viscosity profile shown in **Figure 14**. The following sections present the effect of further reduction of Ca and Mg ions' concentrations (beyond 400 and 25 ppm, respectively) and the effect of reduction of other ions on the viscosity profile of the fracturing fluid.

Table 12 - Compatibility Results of Fluid Prepared with Synthetic Produced Water with Reduced Amounts of Ca and Mg Ions.

Experiment	Na^{+} (mg/l)	K^{+} (mg/l)	$SO4^{-2}$ (mg/l)	Mg^{+2} (mg/l)	Ca^{+2} (mg/l)	Results
1	36,000	1,700	95	700	10,500	Precipitates were observed
2	36,000	1,700	95	100	1,000	Precipitates were observed
3	36,000	1,700	95	50	500	Precipitates were observed
4	36,000	1,700	95	25	400	No precipitates were observed

Table 13 - Composition of the Synthetic Produced Water with the Reduced Amounts of Ca and Mg that the System Can Tolerate.

Ion	Concentration (mg/l)
Ca^{+2}	400
Mg^{+2}	25
Na^{+}	36,000
K^{+}	1,700
SO_4^{-2}	700

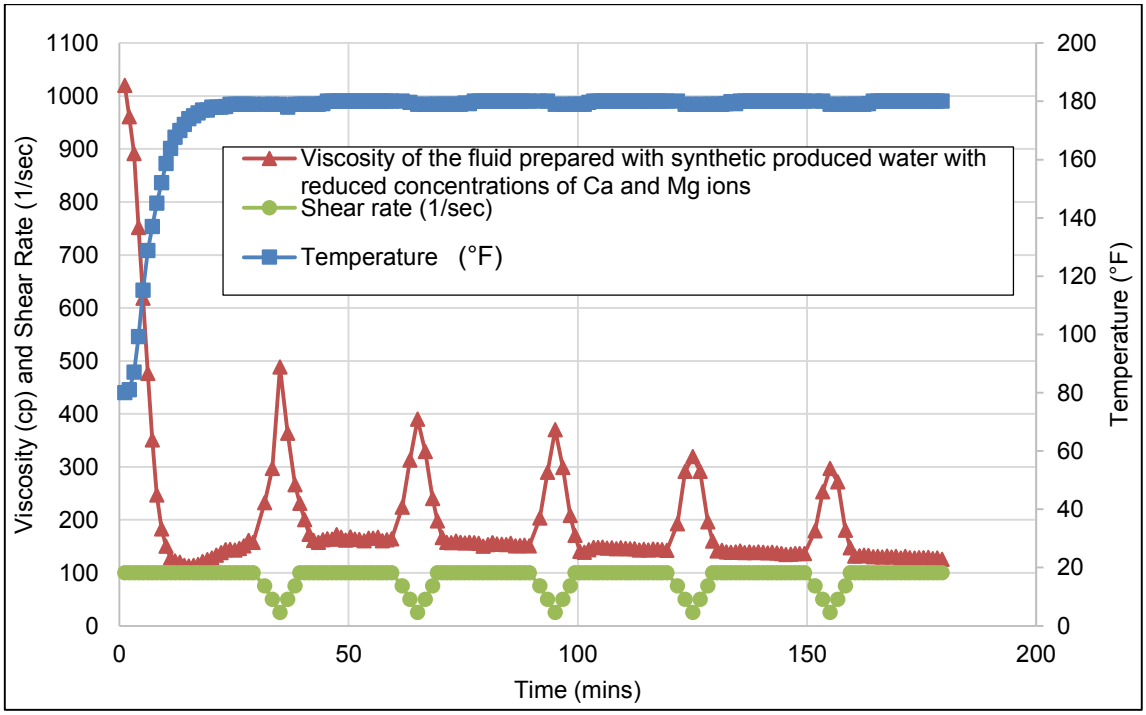


Figure 14 - Viscosity Measurements of the Fluid Prepared with Synthetic Produced Water with Reduced Concentrations of Ca and Mg ions to 400 and 25 ppm, Respectively.

Effect of Reduction of Ions' Concentrations on the Viscosity of the Fracturing Fluid

Studying the effect of reduction of each ion concentration helps designing the required water treatments to qualify the produced water for fracturing fluid formulation. Reduction of water ions concentrations can be done through different water treatments technologies. Filtration, coagulation, electrocoagulation, flocculation, and sedimentation technologies can be used to reduce Total Suspended Solids (TSS), oil and grease content, turbidity, heavy metals, hardness and some divalent cations. Distillation, reverse osmosis, ion exchange, evaporation, and crystallization technologies can be used to reduce Total Dissolved Solids (TDS), divalent cations, and scale-forming ions.

Water cations concentrations are recognized in the literature to affect the viscosity of polymer-based fluids (Bemiller at al. 1992). However, little research was conducted on the effect of each monovalent and divalent cation in the produced water on the viscosity and breaking of fracturing fluids. Sun et al. (2015) studied the effect of different cations on the viscosity of linear (uncrosslinked) fracturing fluid formulated with Hydroxypropyl Guar (HPG).

Haghshenas et al. (2014) studied the effect of different cations on the viscosity of cross-linked guar-based fracturing fluid. However, each ion was studied separately, and tests were done in the absence of fracturing fluid additives.

This part investigates the separate and combined effect of different cations, including: Na, K, Ca, and Mg ions, on the viscosity of the crosslinked fracturing fluid system. The fluid was formulated using natural guar polymer and borate crosslinker, in addition to the fluid additives which are typically used in hydraulic fracturing operations.

Effect of Reduction of Ca and Mg Ions

To study the effect of reduction of calcium ion concentration, the amount of $CaCl_2$ salt in the synthetic produced water was reduced. **Figure 15** shows the viscosity profile of the fluid prepared with synthetic produced water with reduced concentrations of Ca ion.

The reduction of Ca ion concentration from 400 to 200 ppm has improved the viscosity profile and showed no effect when reduced from 200 to 100 ppm. Cations interact with the OH group of the polymer and reduce the dynamic radii of the polymer coils (Sun et al. 2015). Therefore, the reduction of the Ca ion has improved the polymer hydration, and as a result, the viscosity of the fracturing fluid was improved.

The separate effect of the Ca ion alone was also studied (effect of Ca ion in the absence of other ions). DI water with different concentrations of Ca ion was prepared and used to prepare the fracturing fluid. **Figure 16** shows the same effect of Ca ion reduction on the viscosity of the fracturing fluid, which indicates that reduction of Ca ion concentration has the same effect on fluid viscosity in both high and low TDS environments.

The design of the required fracturing fluid viscosity depends on the required fracture height growth and the available surface treating pressure (Montgomery 2013).

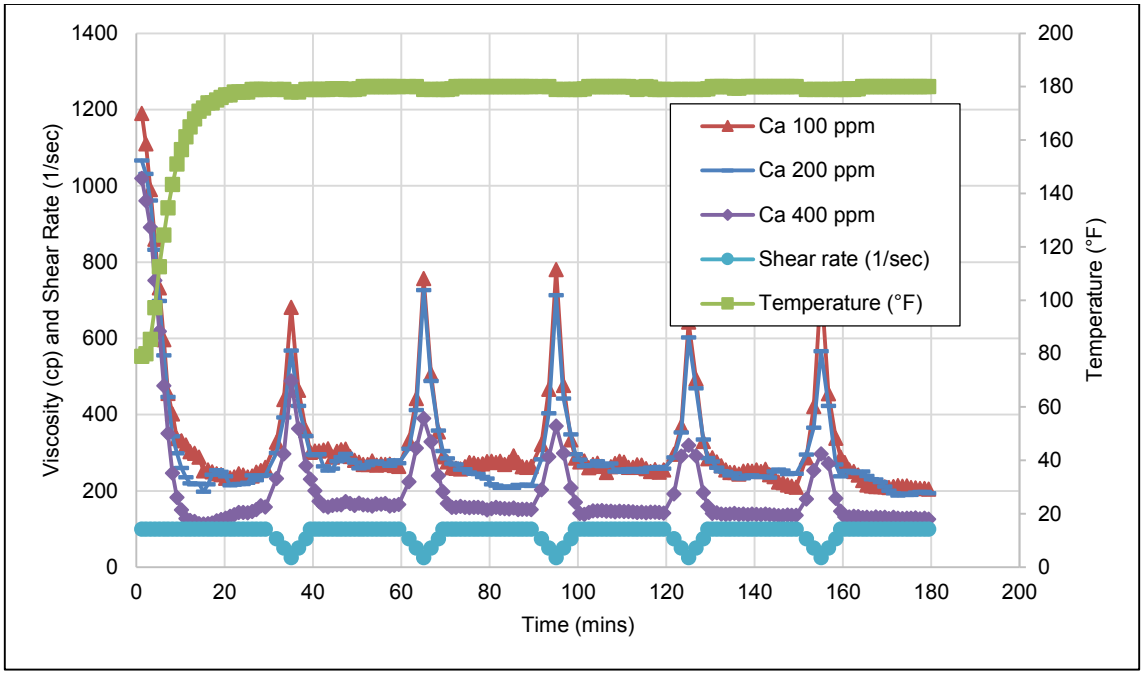


Figure 15 - Viscosity Measurements of the Fluid Prepared with Synthetic Produced Water with Different Concentrations of Ca Ion.

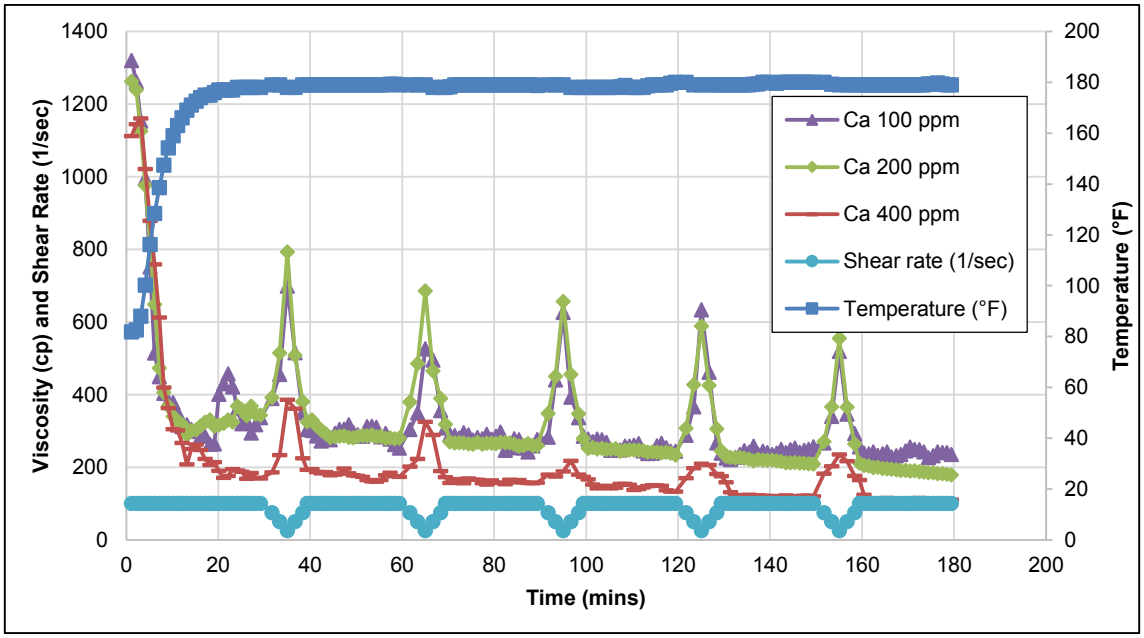


Figure 16 - Viscosity Measurements of the Fluid Prepared with DI Water and Different Concentrations of Ca Ion.

To study the effect of reduction of magnesium ion concentration, the amount of $MgCl_2$ salt in the synthetic produced water was reduced. The viscosity of the fluid prepared with synthetic produced water with reduced concentrations of Mg ion was then measured**.** The results shown in **Figure 17** indicate that the reduction of Mg ion alone from 25 to 12 ppm has shown a very small increment increase in the viscosity of the fracturing fluid, while the reduction from 12 to zero showed no effect. This result is consistent with the findings from Sun et al. (2015). The interaction of Mg ions with the hydroxyl groups of the polymer has no effect on the dynamic radii of the polymer and does not affect the hydration of guar polymer.

The separate effect of Mg ion was also studied (effect of Mg ion in the absence of other ions). DI water with different concentrations of Mg ion was prepared and used to prepare the fracturing fluid. Fracturing fluid viscosity was then measured. The results in **Figure 18** indicate that the fluid containing 25 ppm Mg showed higher viscosity than fluid prepared with no Mg (DI water). The presence of low concentrations of salts in the system enhanced the fluid viscosity because water cations at low concentrations enhance polymer crosslinking and improve fluid viscosity as reported by Bemiller et al. (1992).

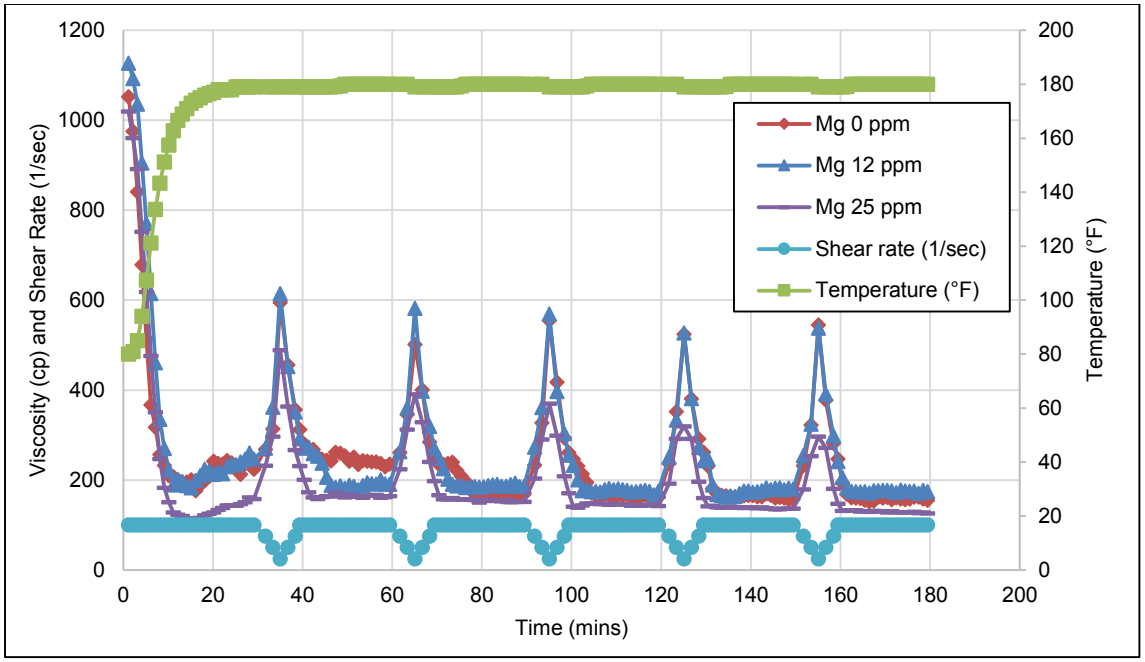


Figure 17 - Viscosity Measurements of the Fluid Prepared with Synthetic Produced Water with Different Concentrations of Mg Ion.

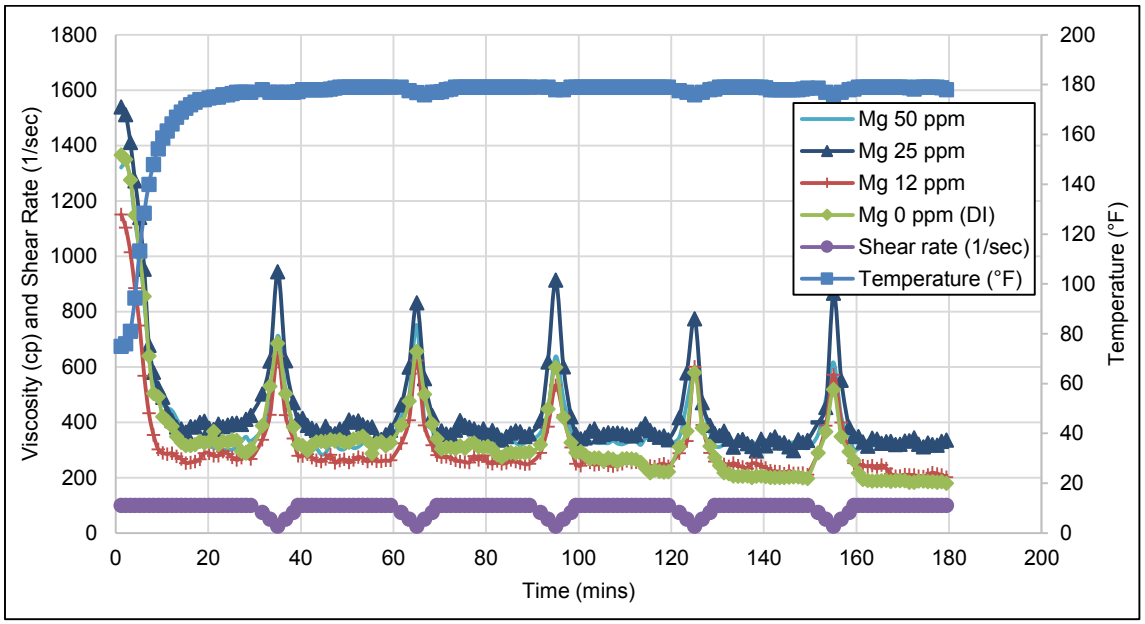


Figure 18 - Viscosity Measurements of the Fluid Prepared with DI Water and Different Concentrations of Mg Ion.

Effect of Reduction of Na and K Ions

Synthetic produced water was prepared with reduced amounts of Na and K ions. The reduction of Na or K ions concentrations to 200 ppm in the presence of other ions showed no effect on the viscosity of the fracturing fluid, as shown in **Figures 19 and 20.** Monovalent cations are known in the literature to reduce polymer hydrolysis in water. Strong salts (NaCl, KCl, etc.) reduce the partial negative charge on the oxygen atom of the OH group when they come into contact with polymer. Therefore, hydrogen bonds between water molecules and the polymer weaken. Hence, fluid viscosity decreases (Das et al. 2014). However, the results showed no effect when Na or K ions were reduced. The effect of each ion alone in DI water was investigated. DI water with different amounts of NaCl was prepared and then fracturing fluid was formulated using each sample. **Figure 21** presents the viscosity of the fluid prepared with DI water with different concentrations of Na ion.

The effect of K ion in DI water was also studied, and the results are shown in **Figure 22**. The results showed the improvement in the fluid viscosity by reducing Na or K ion concentrations. These results are consistent with the findings of Das et al. (2014) and Haghshenase et al. (2014). It was concluded from the results that the presence of Ca and Mg ions in the produced water has suppressed the effect of both Na and K ions on the viscosity of the fracturing fluid.

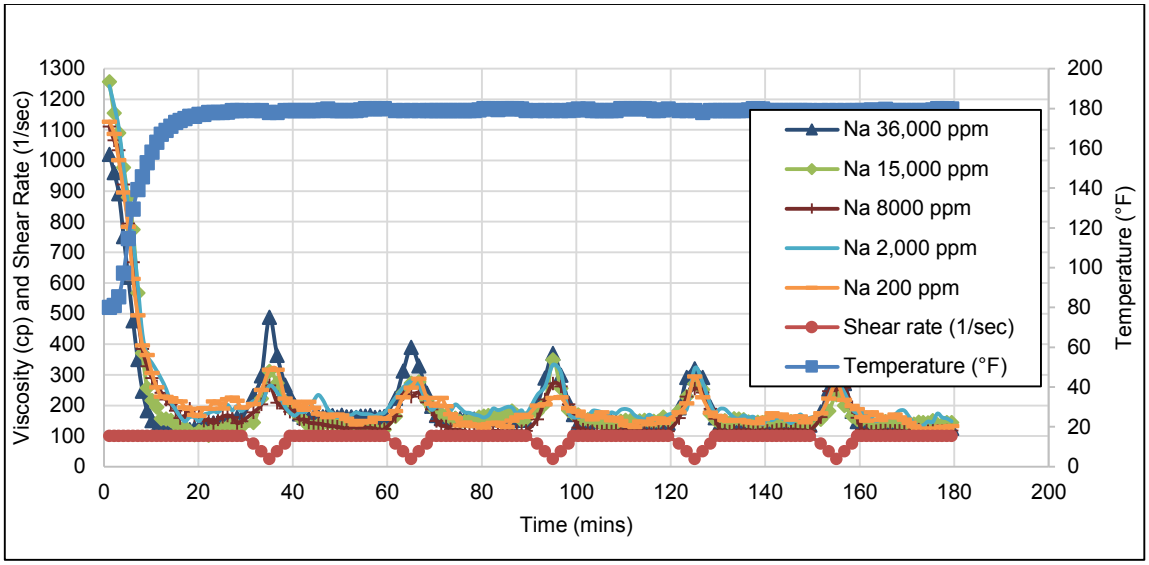


Figure 19 - Viscosity Measurements of the Fluid Prepared with Synthetic Produced Water with Different Concentrations of Na Ion.

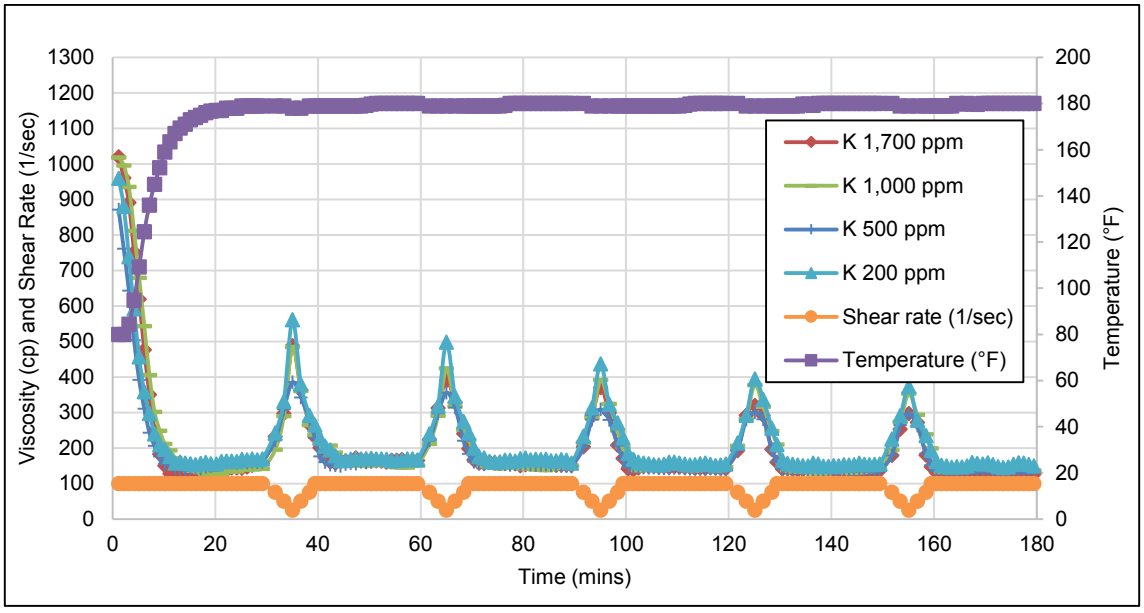


Figure 20 - Viscosity Measurements of the Fluid Prepared with Synthetic Produced Water with Different Concentrations of K Ion.

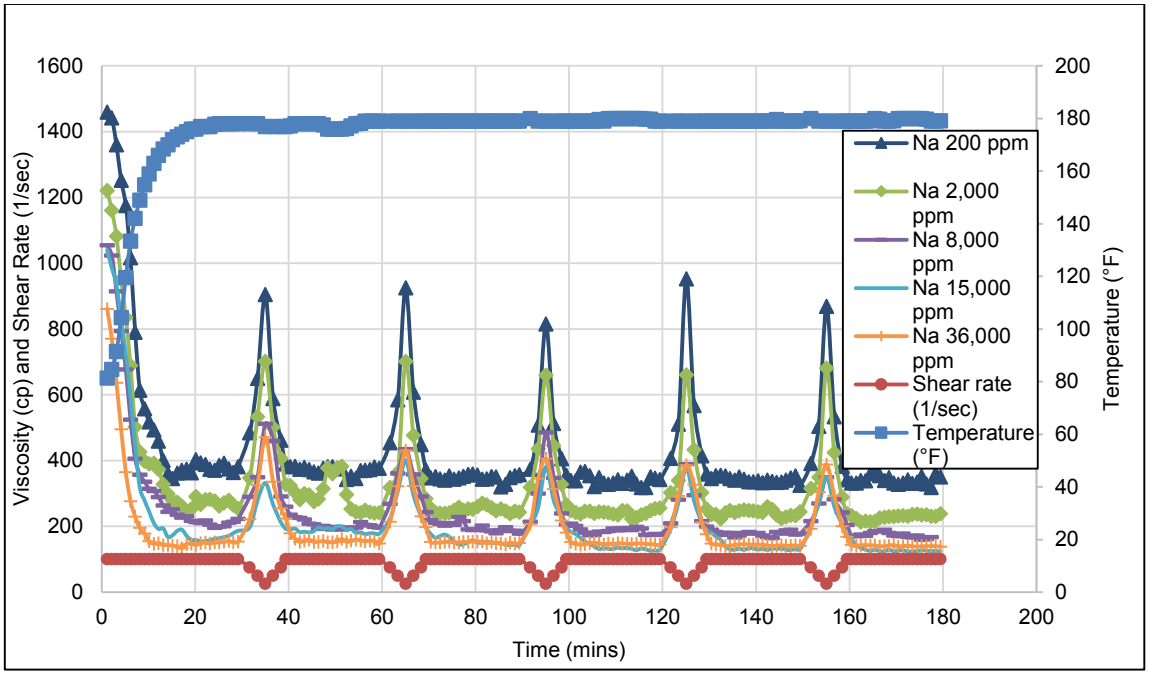


Figure 21 - Viscosity Measurements of the Fluid Prepared with DI Water and Different Concentrations of Na Ion.

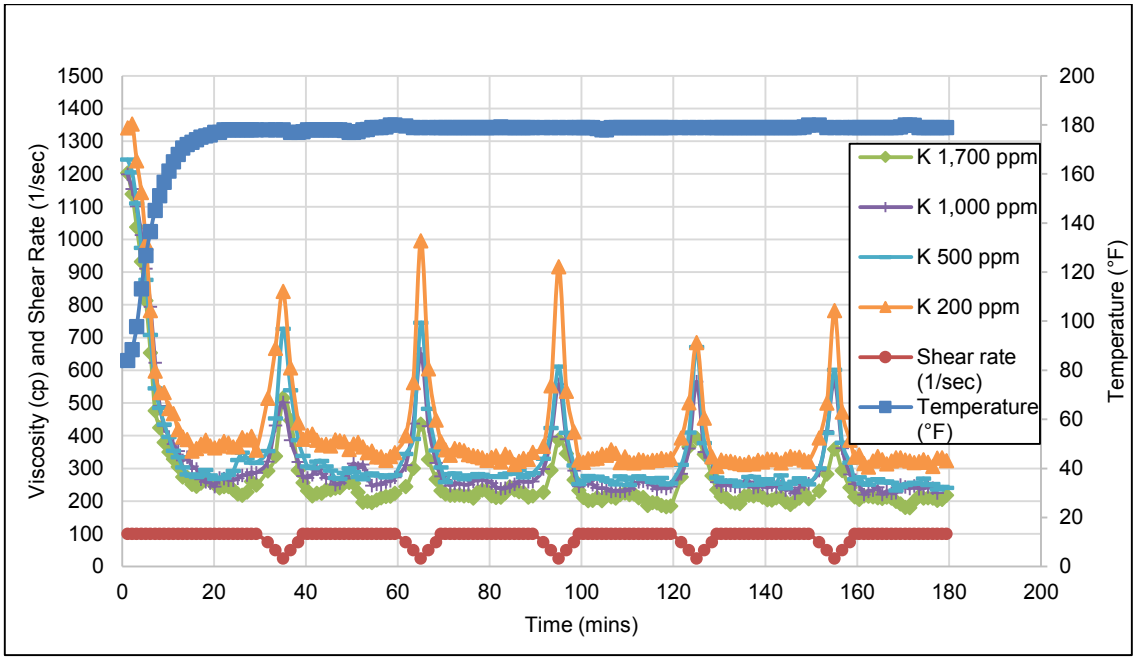


Figure 22 - Viscosity Measurements of the Fluid Prepared with DI Water and Different Concentrations of K Ion.

Effect of Reduction of Sulfate Ion

The reduction of sulfate ions alone in the presence of all other ions showed no effect on the viscosity of the fracturing fluid, as shown in **Figure 23.** A high sulfate concentration in produced water could cause premature fluid breaking (Huang et al. 2005). However, produced water contains only 95 ppm sulfate ion, and hence, the effect of the reduction of sulfate ions was quite small and could not be observed.

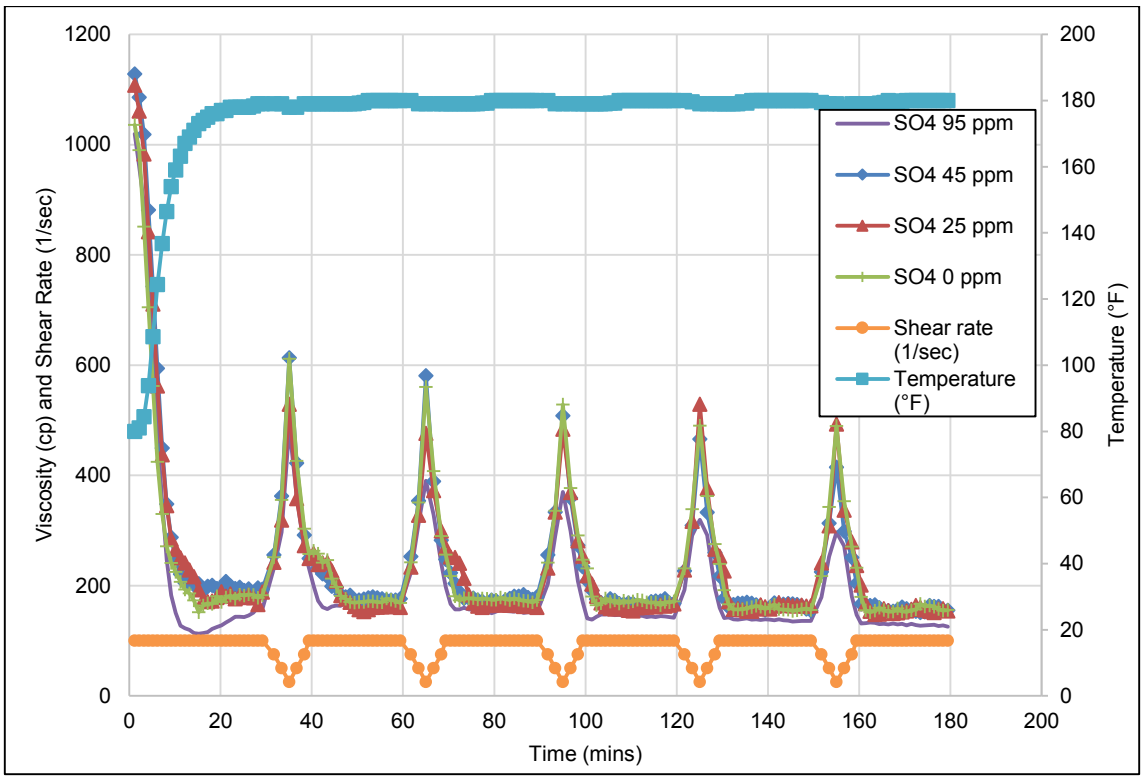


Figure 23 - Viscosity Measurements of the Fluid Prepared with Synthetic Produced Water with Different Concentrations of SO_4 Ion.

Fluid Breaking Test

Fluid breaker was added to the formulation of the fracturing fluid to test the breaking of the fluid. The breaker used was encapsulated ammonium persulfate and added at the concentration of 1 ppt (lb/1000g). Encapsulation decomposes and releases the breaker at 120 °F. Synthetic produced water with reduced Ca and Mg ions concentrations (400 and 25 ppm, respectively) was used to prepare the fracturing fluid with the presence of the breaker. The viscosity of the fluid was then measured at shear rate of 100 sec^{-1} and temperature of 180 °F. **Figure 24** shows the reduction of the fluid viscosity to 20 cp after 70 minutes, which indicates complete fluid breaking. The results indicated the proper breaking of the fluid in spite of the high monovalent and divalent cations concentrations present in the system.

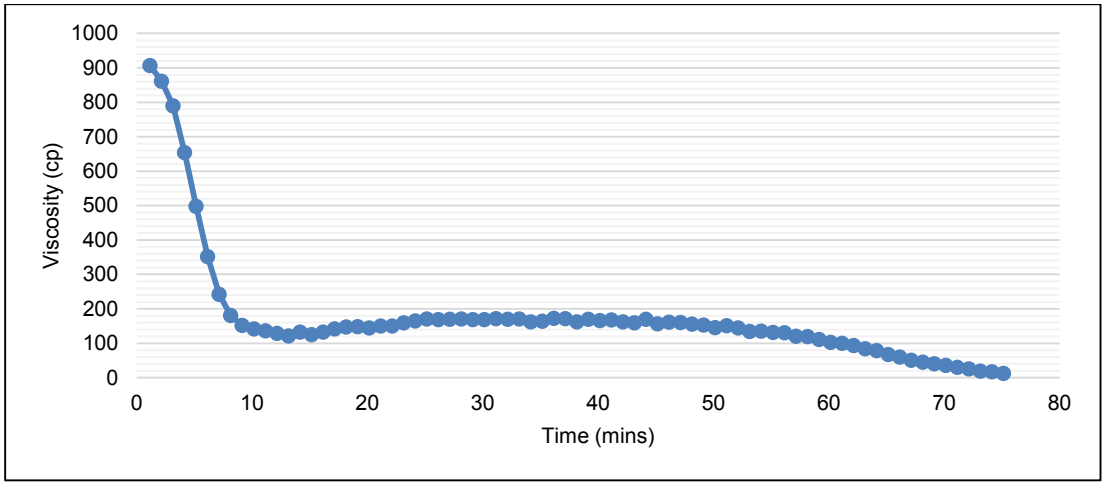


Figure 24 - Viscosity Measurements of the Fluid Prepared with Synthetic Produced Water with Ca and Mg Ion Concentrations of 400 and 25 ppm, respectively, in the Presence of Fluid Breaker at 100 sec^{-1} and 180 °F.

The Effect of Adding Different Chelating Agents to the Fracturing Fluid System

Chelating agents are compounds having the ability to form metal complexes with divalent and trivalent cations that are soluble in water. Chelating agents have different applications in various industries. They are used as fertilizers to provide micronutrients for plants, used in water treatment to prevent scale formation, and used as a heavy metal detoxification agent in medicine and food industry. In the oil and gas industry, chelating agents have been used for different purposes such as inorganic scale removal, iron control, and recently, as stand-alone stimulation for matrix acidizing (Taylor and Nasr-El-Din, 1999, Fredd and Fogler, 1998).

The objective of this part is to study the effect of using different chelating agents on the precipitate formation and on the viscosity of the fracturing fluid. The main purpose of the use of chelating agents is to increase the tolerance of the fluid system to the divalent cations, and as a result, prevent the formation of precipitate, and maintain high fracturing fluid viscosity. Five chelating agents were tested, includes HEDTA (hydroxyethylethylene diamine triacetic acid tri-Sodium salt), GLDA (glutamic acid diacetic acid tetra-sodium salt), di-sodium-EDTA (ethylendiamine tetra acetic acid di-sodium salt), di-ammonium-EDTA (ethylendiamine tetra acetic acid di-ammonium salt), and Na-gluconate (gluconic acid sodium salt). The chemical structure of each chelating agent is shown in **Figure 25.**

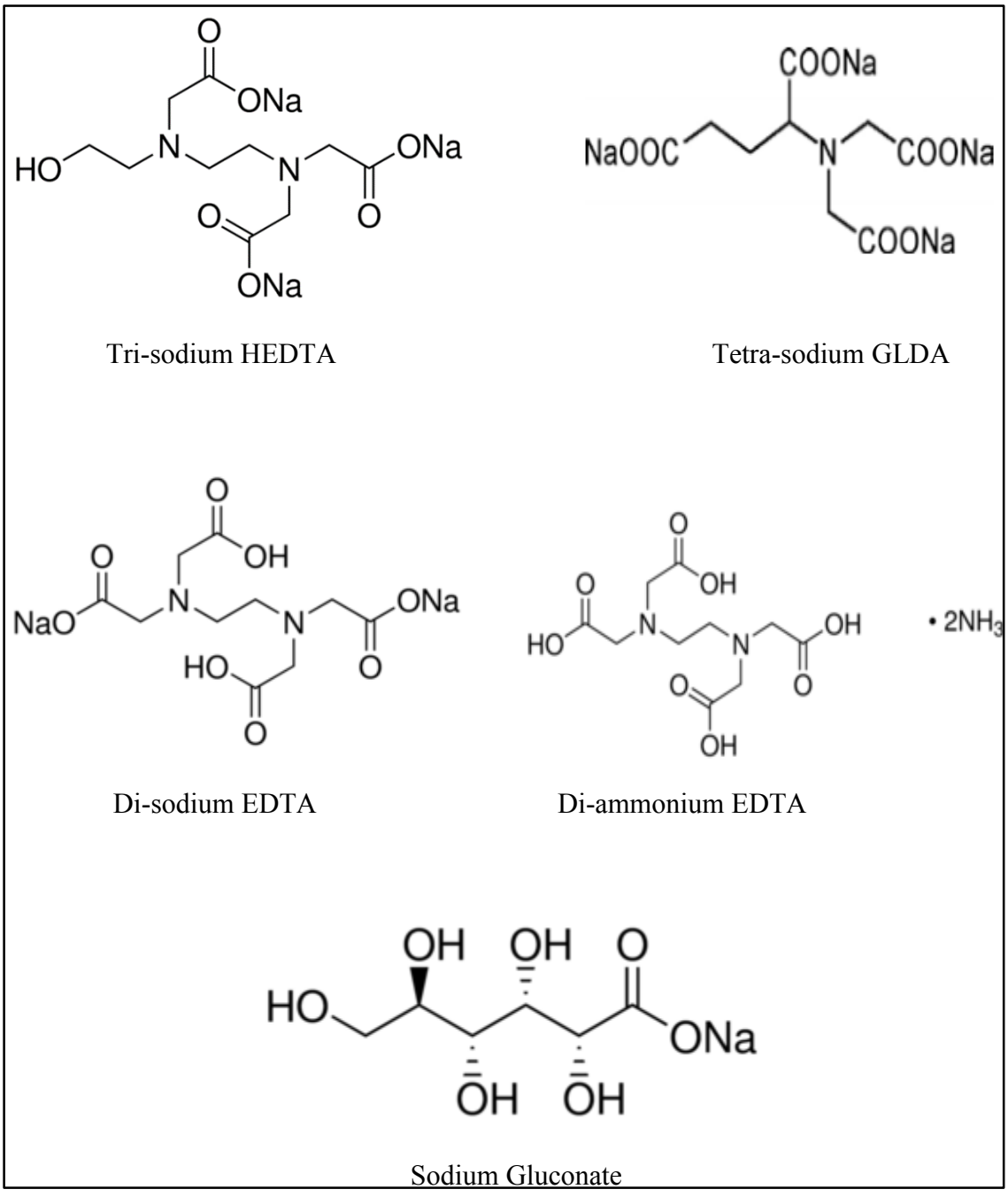


Figure 25 - Chemical Structures of Different Chelating Agents.

The Effect of Adding HEDTA to the Fracturing Fluid System

Synthetic produced water was prepared and the fracturing fluid was prepared with the addition of different concentrations of the HEDTA. Compatibility tests were done to determine the concentration of the Ca and Mg ions that the system can tolerate. Na, K, SO_4 concentrations were kept constant and Ca and Mg ions concentrations were reduced gradually until no precipitations were observed. Viscosity tests were performed to evaluate the fracturing fluid viscosity after the addition of the chelating agent.

Different concentrations of HEDTA were tested, includes 1 wt%, 2.5 wt%, 5 wt%. Results of the compatibility tests after the addition of 1 wt% to the fluid system are shown in **Table 14,** which indicated that the addition of 1 wt% of the HEDTA has increased the Ca and Mg concentrations that the system can tolerate from 400 and 25 ppm, respectively, to 1000 and 100 ppm, respectively. The use of HEDTA has reduced Ca and Mg ions precipitations due to its sequestration effect on the divalent cations and the formation of stable complexes which are soluble in water (Means et al. 2003).

Viscosity of the fluid prepared with synthetic produced water with reduced Ca and Mg ions concentrations to 1,000 and 100 ppm, respectively, and with the addition of 1 wt% HEDTA to the fluid system was measured and results are shown in **Figure 26.** The viscosity profile indicated an average viscosity value of 150 cp at 100 sec^{-1} shear rate, which indicates that the addition of HEDTA has no negative effect on the viscosity of the fracturing fluid.

Table 14 - Compatibility Results of Fluid Prepared with Synthetic Produced Water with 1 wt% HEDTA and Reduced Amounts of Ca and Mg Ions.

Experiment	Na^{+} (mg/l)	K^{+} (mg/l)	$SO4^{-2}$ (mg/l)	Mg^{+2} (mg/l)	Ca^{+2} (mg/l)	Results
1	36,000	1,700	95	700	10,500	Precipitates were observed
2	36,000	1,700	95	400	5,000	Precipitates were observed
3	36,000	1,700	95	200	2,500	Precipitates were observed
4	36,000	1,700	95	100	1000	No precipitates were observed

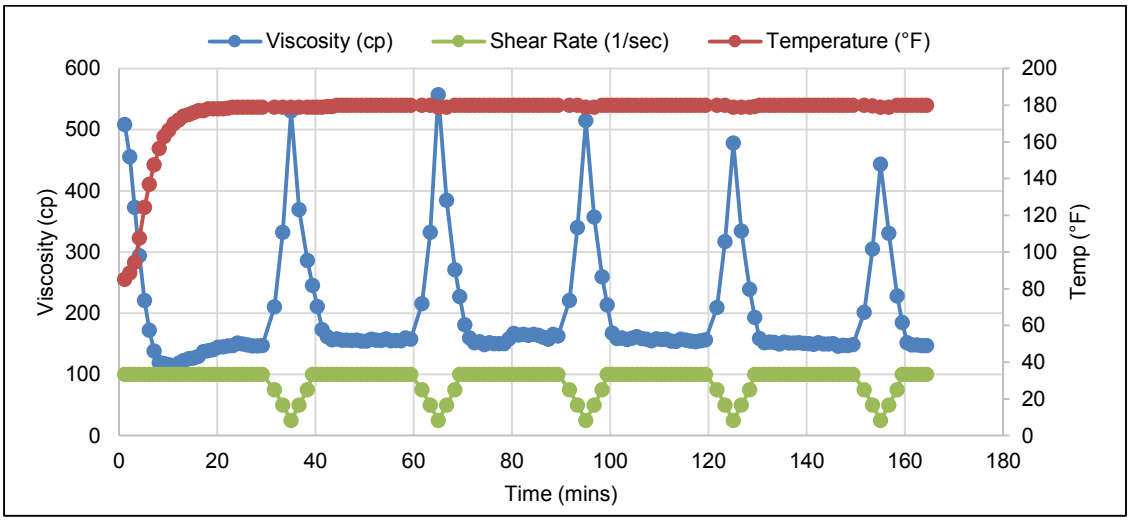


Figure 26 - Viscosity Measurements of the Fluid Prepared with 1 wt% HEDTA, 1,000 ppm Ca and 100 ppm Mg.

Compatibility tests were repeated with the same procedures with HEDTA concentration of 2.5 wt%. Results in **Table 15** indicated the increase in Ca and Mg concentrations that the system can tolerate to 2,500 and 200 ppm, respectively.

Table 15 - Compatibility Results of Fluid Prepared with Synthetic Produced Water with 2.5 wt% HEDTA and Reduced Amounts of Ca and Mg Ions.

Experiment	Na^{+} (mg/l)	K^{+} (mg/l)	$SO4^{-2}$ (mg/l)	Mg^{+2} (mg/l)	Ca^{+2} (mg/l)	Results
1	36,000	1,700	95	700	10,500	Precipitates were observed
2	36,000	1,700	95	400	5,000	Precipitates were observed
3	36,000	1,700	95	200	2,500	No Precipitates were observed

Viscosity of the fluid prepared with synthetic produced water with reduced Ca and Mg ions concentrations to 2,500 and 200 ppm, respectively, and with the addition of 2.5 wt% HEDTA to the fluid system was measured and results are shown in **Figure 27**. The viscosity profile indicated an average viscosity value of 125 cp at 100 sec^{-1} shear rate.

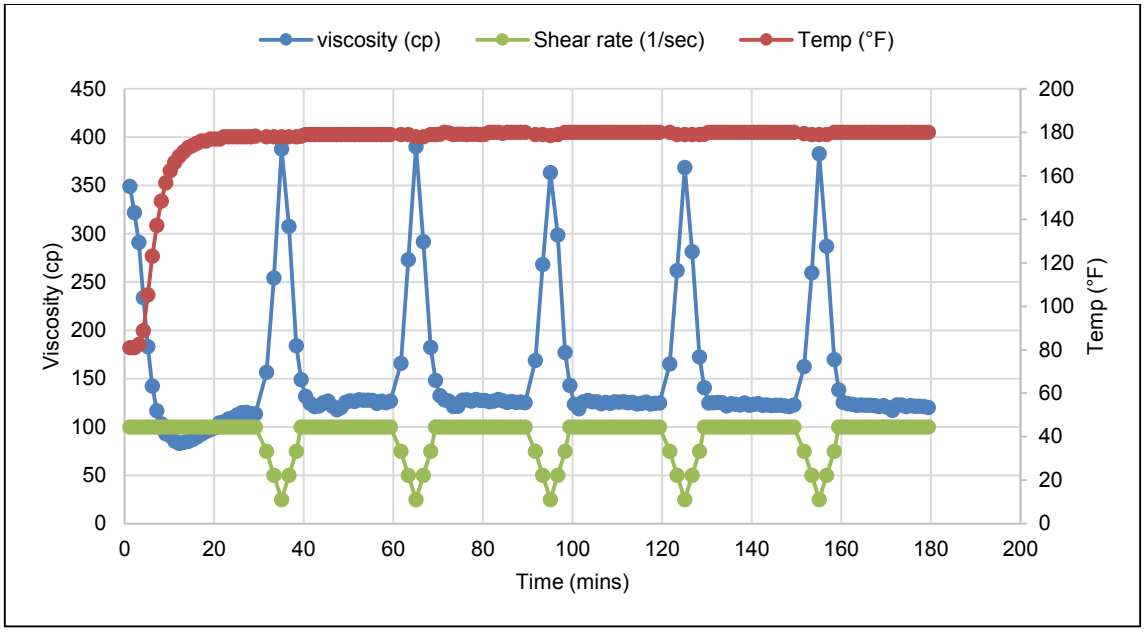


Figure 27 - Viscosity Measurements of the Fluid Prepared with 2.5 wt% HEDTA, 2,500 ppm Ca and 200 ppm Mg.

The effect of increasing the HEDTA concentration to 5 wt% was also studied. Compatibility tests were repeated with the same procedures with HEDTA concentration of 5 wt%. Results in **Table 16** indicated the increase in Ca and Mg concentrations that the system can tolerate to 5,000 and 400 ppm, respectively.

Table 16 - Compatibility Results of Fluid Prepared with Synthetic Produced Water with 5 wt% HEDTA and Reduced Amounts of Ca and Mg Ions.

Experiment	Na^{+} (mg/l)	K^{+} (mg/l)	$SO4^{-2}$ (mg/l)	Mg^{+2} (mg/l)	Ca^{+2} (mg/l)	Results
1	36,000	1,700	95	700	10,500	Precipitates were observed
2	36,000	1,700	95	400	5,000	No Precipitates were observed

Viscosity of the fluid prepared with synthetic produced water with reduced Ca and Mg ions concentrations to 5,000 and 400 ppm, respectively, and with the addition of 5 wt% HEDTA to the fluid system was measured and results are shown in **Figure 28**. Results shows that the addition of 5 wt% of HEDTA has prevented the precipitation of Ca and Mg ions, however, the initial viscosity was found to be 130 cp and has decreased to 20 cp after 50 minutes. The reduction in the fluid viscosity is due to the high concentration of Ca and Mg ions in solution which negatively affects the fluid viscosity (Sun et al. 2015, Haghshenas et al. 2014).

Figures 29 and 30 summarize the effect of HEDTA on the concentrations of Ca and Mg ions that the system can tolerate, and its effect on the average viscosity of the fracturing fluid.

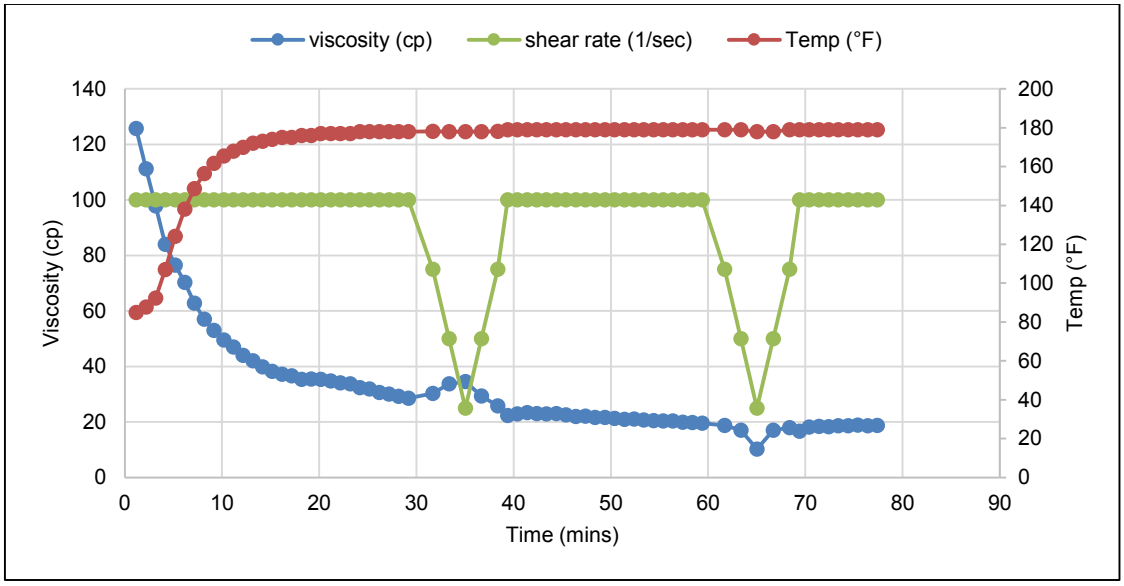


Figure 28 - Viscosity Measurements of the Fluid Prepared with 5 wt% HEDTA, 5,000 ppm Ca and 400 ppm Mg Ion.

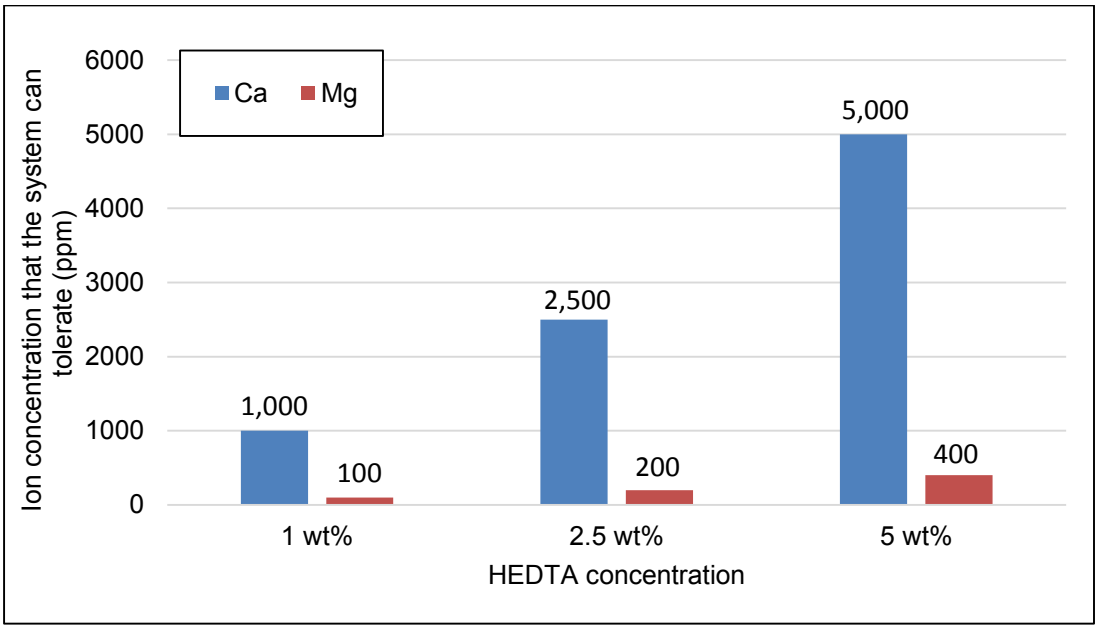


Figure 29 – The Effect of HEDTA on the Concentrations of Ca and Mg Ions that the System Can Tolerate.

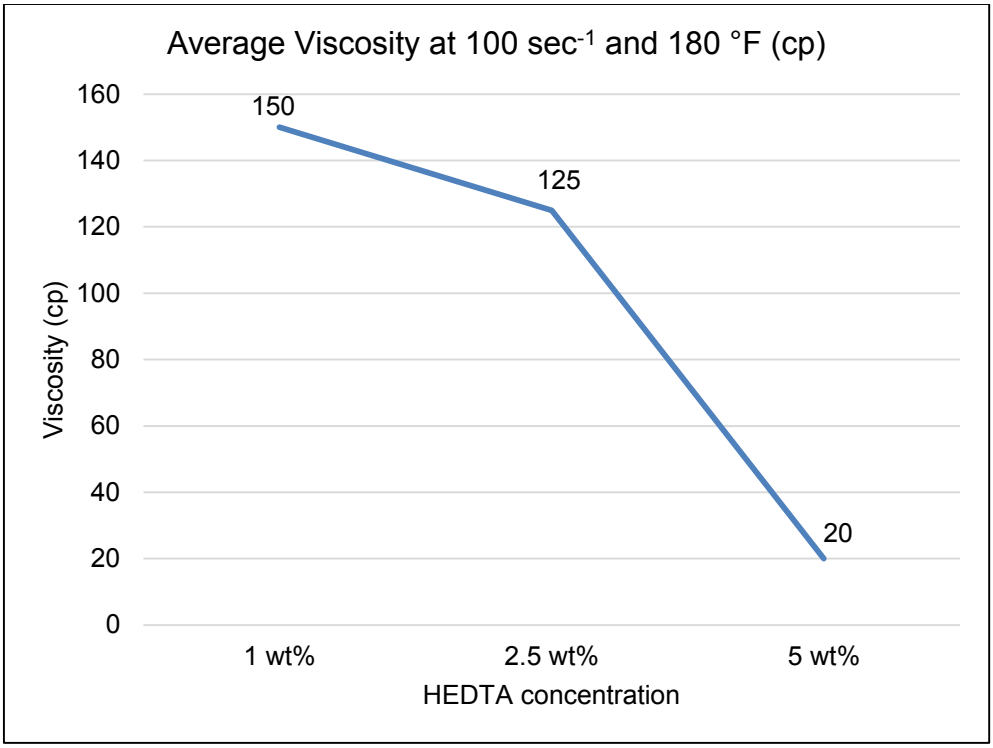


Figure 30 – The Effect of HEDTA on the Viscosity of the Fracturing Fluid.

The Effect of Adding GLDA to the Fracturing Fluid System

GLDA is a chelating agent that consists of only one nitrogen atom. Its major part is derived from monosodium glutamate (MSG). Monosodium glutamate is obtained by corn sugar fermentation and is considered a renewable raw material. In addition, the source of carbon atom in the GLDA is biologically-based, as a result, the GLDA is considered as the only chelating agent with green carbon atoms (Kolodynska 2010, LePage et al. 2011).

Synthetic produced water was prepared and fracturing fluid was prepared with the addition of different concentrations of the GLDA. Compatibility tests were done to determine the concentration of the Ca and Mg ions that the system can tolerate. Na, K,

SO_4 concentrations were kept constant and Ca and Mg ions concentrations were reduced gradually until no precipitations were observed. Viscosity tests were performed to evaluate the fracturing fluid viscosity after the addition of the chelating agent.

Different concentrations of GLDA were tested, includes 1 wt%, 2.5 wt%. Results of the compatibility tests after the addition of 1 wt% to the fluid system are shown in **Table 17** which indicated that the addition of 1 wt% of the GLDA has increased the Ca and Mg concentrations that the system can tolerate from 400 and 25 ppm, respectively, to 1,000 and 100 ppm, respectively. The use of GLDA has reduced Ca and Mg ions precipitations due to its combination with the divalent cations and the formation of water soluble complexes.

Table 17 - Compatibility Results of Fluid Prepared with Synthetic Produced Water with 1 wt% GLDA and Reduced Amounts of Ca and Mg Ions.

Experiment	Na^+ (mg/l)	K^+ (mg/l)	$SO4^{-2}$ (mg/l)	Mg^{+2} (mg/l)	Ca^{+2} (mg/l)	Results
1	36,000	1,700	95	700	10,500	Precipitates were observed
2	36,000	1,700	95	400	5,000	Precipitates were observed
3	36,000	1,700	95	200	2,500	Precipitates were observed
4	36,000	1,700	95	100	1,000	No precipitates were observed

Viscosity of the fluid prepared with synthetic produced water with reduced Ca and Mg ions concentrations to 1,000 and 100 ppm, respectively, and with the addition of 1 wt% GLDA to the fluid system was measured and results are shown in **Figure 31**. The viscosity profile indicated an average viscosity value of 150 cp at 100 sec^{-1} shear rate, which indicates that the addition of GLDA has no negative effect on the viscosity of the fracturing fluid.

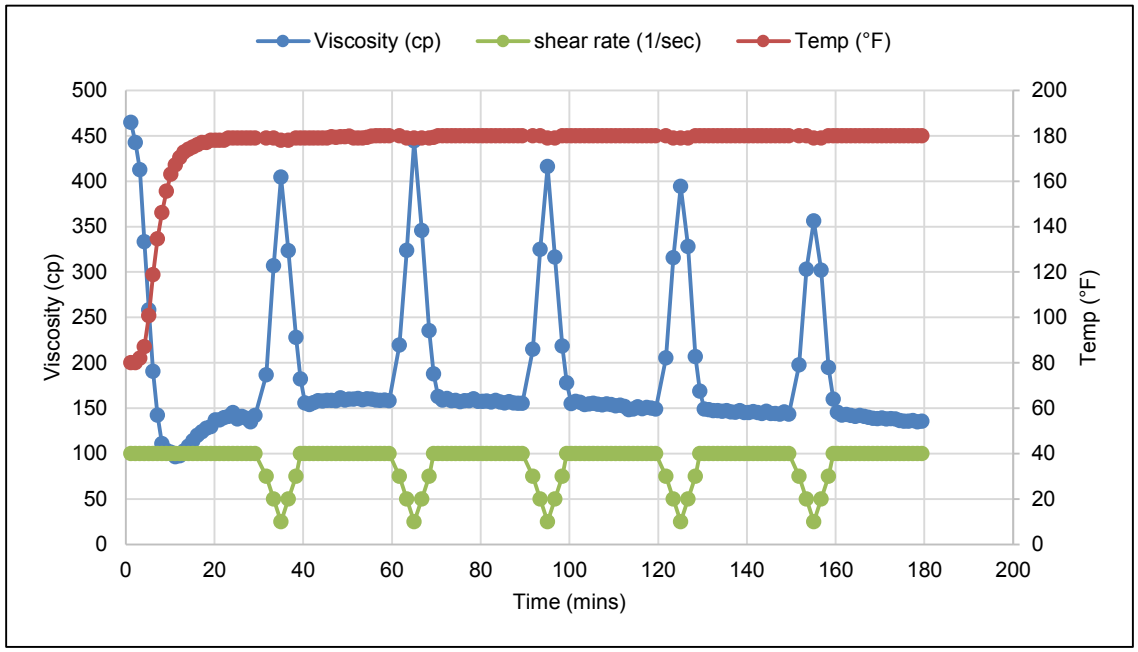


Figure 31 - Viscosity Measurements of the Fluid Prepared with 1 wt% GLDA, 1,000 ppm Ca and 100 ppm Mg.

Compatibility tests were repeated with the same procedures with GLDA concentration of 2.5 wt%. Results in **Table 18** indicated that the increase in GLDA concentration has not increased the system tolerancy to Ca and Mg ions as shown in **Figure 32**. The concentrations of Ca and Mg ions that the system can tolerate is the same as the values obtained by using 1 wt% GLDA and further increase in the GLDA concentration has no effect. This indicates the limited effect of GLDA chelation to Ca and Mg ions in solution to certain concentration.

Table 18 - Compatibility Results of Fluid Prepared with Synthetic Produced Water with 2.5 wt% GLDA and Reduced Amounts of Ca and Mg Ions.

Experiment	Na^{+} (mg/l)	K^{+} (mg/l)	$SO4^{-2}$ (mg/l)	Mg^{+2} (mg/l)	Ca^{+2} (mg/l)	Results
1	36,000	1,700	95	700	10,500	Precipitates were observed
2	36,000	1,700	95	400	5,000	Precipitates were observed
3	36,000	1,700	95	200	2,500	Precipitates were observed
4	36,000	1,700	95	100	1,000	No Precipitates were observed

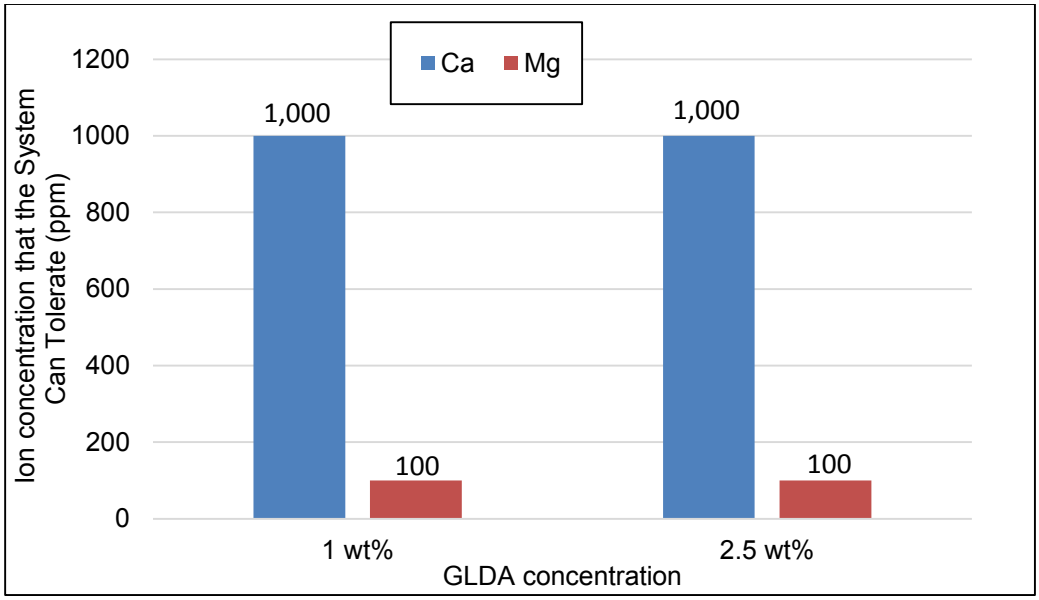


Figure 32 - The Effect of GLDA on the Concentrations of Ca and Mg Ions that the System Can Tolerate.

The Effect of Di-Sodium EDTA, Di-Ammonium EDTA, and Sodium Gluconate

EDTA (ethylenediaminetetraacetic acid) is an amino carboxylic acid chelating agent that has the ability to dissolve calcite. Several studies showed the ability of EDTA to be used as a stand-alone stimulation fluid for limestone matrix acidizing (Fredd and Fogler,1998). Gluconic acid and its salts have been used in many applications due to their favorable chemical and physical properties. They are noncorrosive, nontoxic, nonvolatile, and readily biodegradable (Ramachandran et al. 2006).

The objective of this part is to study the effect of using different concentrations of di-sodium EDTA, di-ammonium EDTA, and sodium gluconate on the formation of the precipitations and on the viscosity of the fracturing fluid.

Results showed that the three chelating agents have the same effect on the fracturing fluid system. The addition of 1 wt% of any of the three chemicals has resulted in a rapid reduction in the initial value of the fracturing fluid viscosity. The addition of 1 wt% a has reduced the initial fluid viscosity to less than 20 cp. **Figure 33** shows the viscosity profile of the fluid prepared with synthetic produced water with Ca and Mg concentrations of 1,000 and 100, respectively, using the three different chelating agents.

Reduction of the concentration of each chelating agent concentration to 0.5 wt% has been investigated. However, same results were obtained as the 1 wt% concentration. **Figure 34** shows the viscosity profile for the three chelating agents.

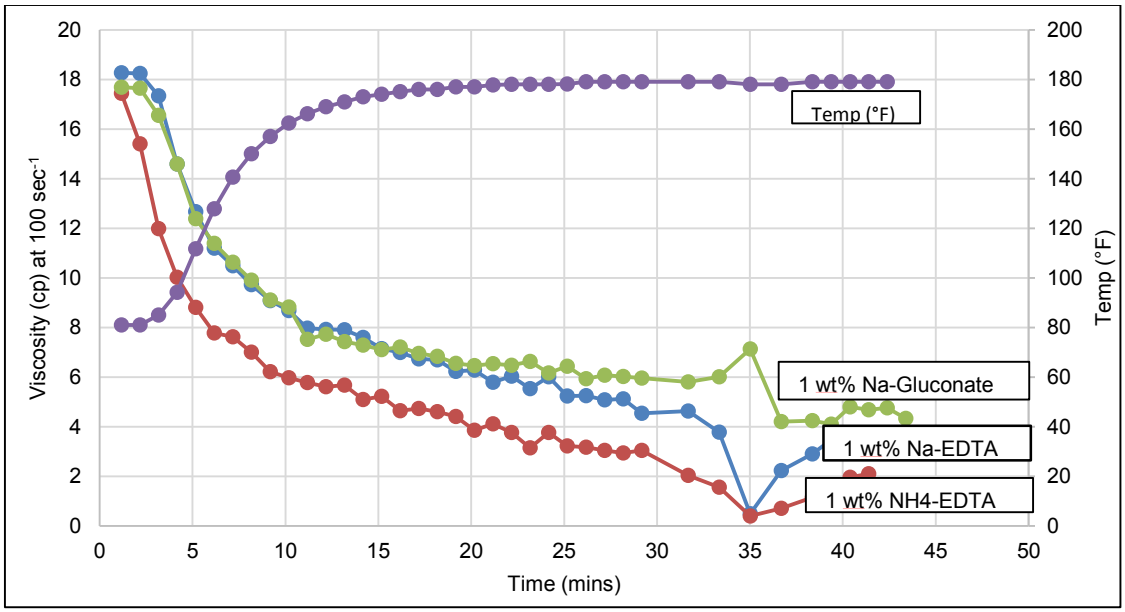


Figure 33 - Viscosity Measurements of the Fluid Prepared with 1 wt% of the Chelating Agent, 1,000 ppm Ca and 100 ppm Mg.

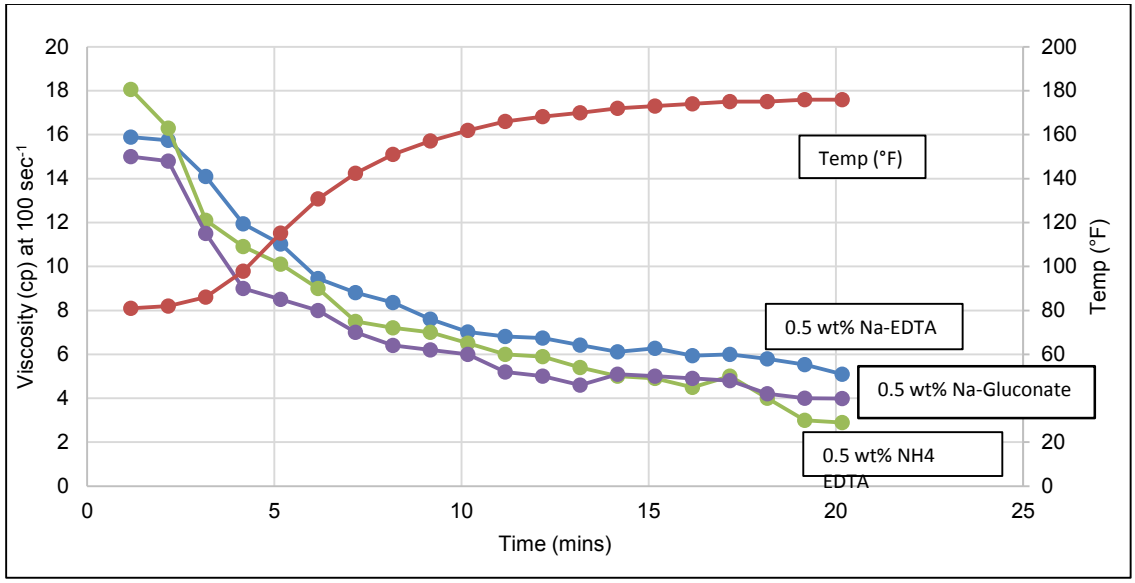


Figure 34 - Viscosity Measurements of the Fluid Prepared with 0.5 wt% of the Chelating Agent, 1,000 ppm Ca and 100 ppm Mg.

The addition of di-sodium EDTA showed a breaking effect on the viscosity of the fracturing fluid. Measuring the pH value of the fluid before and after adding the chelating agent has indicated the reduction of pH value from 11 to 3.8. The reduction of pH value has negatively affected the viscosity of the fluid due to the reduction in the concentration of borate ions which are the main ion for crosslinking the polymer molecules. The crosslinking of polymer molecules is the main mechanism of building high viscosity values. The concentration of the borate ion in the solution depends on the pH value as reported by (Harris, 1993). **Figure 35** shows the relation between the pH value and borate ion concentration in a solution of boric acid, as a source for the borate ion, and 2 wt% KCl (Harris, 1993). The pH value required for adequate crosslinking should be more than 10. This explains the reduction of the fluid viscosity after the addition of the di-sodium EDTA.

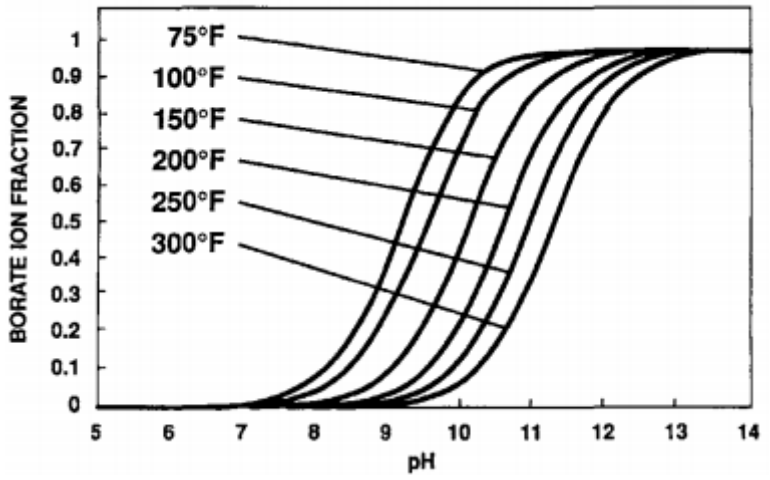
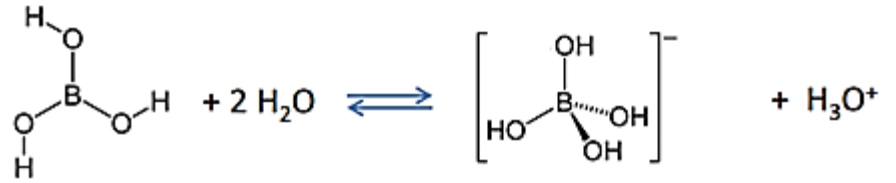


Figure 35 - Borate Ion Concentration as a Function of the pH Value.

The source of borate ions in the system is the reaction between boric acid (the crosslinker) and water as follows. The molecular structure of guar crosslinked molecules was shown earlier in **Figure 7**.



Sodium gluconate and di-ammonium EDTA showed a different mechanism of breaking the fracturing fluid viscosity. Measuring the pH value before and after the addition of each of them indicated initial and final pH values between 10 and 11 which is considered as adequate environment for the borate crosslinker. The breaking effect of the sodium gluconate and di-ammonium EDTA is explained by the ability of the two chelating agents to form complexes with the boron ion, which is the main ion in the

borate ion that crosslink the polymer molecules together. Chelating agents have the ability to form water soluble metal complexes with divalent and trivalent cations. Boron is a trivalent metalloid that could be sequestered using the chelating agents. The combination between the boron ion and the chelating agent could lead to breaking the bonds between the polymer molecules and thus greatly reduce the fluid viscosity.

The ability of sodium gluconate to break the fracturing fluid viscosity was stated in the literature by (Crews, 2007). The author considered the sodium gluconate as a chemical belongs to Polyols compounds. However, no details were mentioned about the mechanism and the conditions for its breaking effect.

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

The objective of this study was to experimentally evaluate the use of produced water to formulate guar-based crosslinked fracturing fluid. The results indicated that the produced water could cause formation damage if used directly to formulate the hydraulic fracturing fluid. Results further showed that precipitations could be prevented if the produced water is diluted with fresh water, or treated to reduce the concentration of scale-forming ions. Furthermore, reduction of some water cations concentration was found to enhance the viscosity of the fracturing fluid. Based on the results obtained, the following conclusions were drawn:

1. Direct use of produced water to formulate the fracturing fluid could cause the precipitation of Ca and Mg ions.
2. Produced water could be used to formulate the fracturing fluid if diluted with fresh water 25 times.
3. Precipitations could be prevented if the produced water is treated and the Ca and Mg ions were reduced to 400 and 25 ppm, respectively.
4. Further reduction of Ca and Mg ions could enhance the fracturing fluid viscosity.
5. Reduction of Na and K ions was found to affect fracturing fluid viscosity only in the absence of divalent cations, and showed no effect in the presence of high divalent cations concentration.

6. The high salt content of produced water showed no effect on fracturing fluid breaking.

The effect of chelating agents on the tolerancy of the system to Ca and Mg ions and on the viscosity of the fracturing fluid were also studied. Results indicated the following:

1. The use of HEDTA and GLDA increased the system tolernacy to Ca and Mg ions and maintained adequate fracturing fluid viscosity.
2. Sodium gluconate, di-sodium EDTA, and di-ammonium EDTA showed a breaking effect on the viscosity of the fracturing fluid and shouldn't be added to the fluid formulation.

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